

# Three-Dimensional Printing of Hierarchical Porous Architectures

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Primary CNF Tools Used: Leica supercritical dryer; SEMs, microscopes, ABM aligner, lithography room

## Abstract:

Concurrent advances in nanomaterial synthesis and additive 3D manufacturing have created a rich and exciting opportunity space fabricate novel materials and devices. Particularly, integrating high surface area porous materials into structured devices for energy storage, separation system, catalysis and sensing presents interesting scientifically interesting and technologically relevant challenges. Here, we introduce three-dimensional printing of superstructures with multi-level porous networks starting from simple light-controllable building blocks, zirconia core with 12 methacrylic acid ligands. We introduce a new photoresin based on photoresponsive ligand on inorganic core to enable a bottom-up route to program structure, composition and function across seven orders of magnitude in length scale! As a proof of concept, we demonstrate a 3D printed biomimetic artificial leaf with nature-comparable framework and functions such as carbon dioxide capture. This work demarks a significant step forward in creating programmable hierarchical mesoporous structures that approach the complexity common in natural systems.

## Summary of Research:

Porous materials are notoriously difficult to process, so synthetic materials are mostly in the form of powder but lacking the mesoscale structure found in natural systems. We introduce photoresponsive ligand on inorganic core (PLIC) design to overcome outstanding challenges related to the processing of porous materials in programmable hierarchical structures. We demonstrate a novel method for generating hierarchical 3D superstructures with nano- to macroscopic controls by three-dimensional (3D) printing of  $\sim 2$  nm metal-containing building units into centimeter-level predesigned complex monoliths.

Figure 1 schematically illustrates how the hierarchical fabrication approach provides a bottom-up route connecting seven orders of magnitude in length scale. Analogous to metal-organic-frameworks (MOFs), the intra-particle and inter-particle pores will form when the PLIC nano-units are connected together. Unlike solvothermal reactions traditionally on MOFs, our fabrication scheme uses light to spatially program where the porous materials are formed. With PLIC as 3D printing inks, we can manipulate predesigned structures in different length scale on a single printing

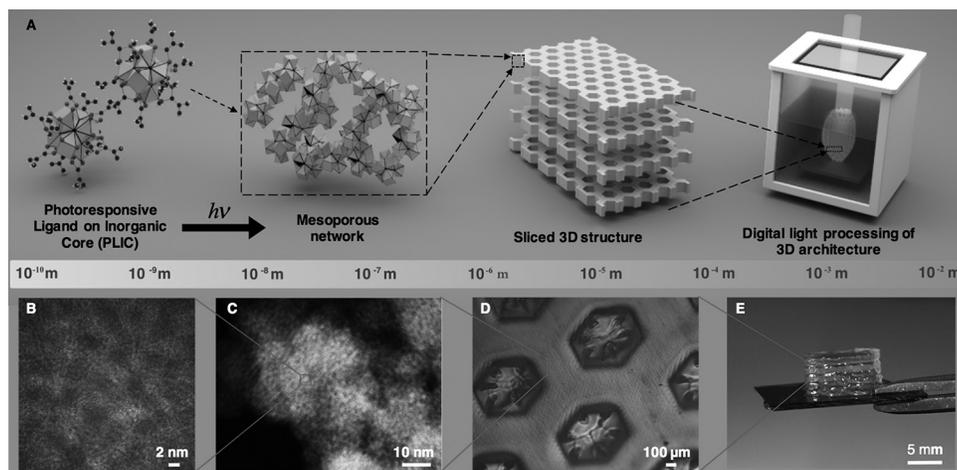


Figure 1: Three-dimensional printing PLIC assembly. (A) Schematic representation of multi-level control in the printing process. PLIC materials are used as the building units and structured by series of 2D UV images in the 3D printer. (B) The unit cell of zirconia inorganic nanocrystal with methacrylic acid surface ligands. (C) Formation of pores via connecting the building units. (D) An example of printed structure showing shape control for each layer. (E) Centimeter scale resulting parts with layer by layer stacking. See full color version on pages xxviii-xxix.

procedure. This process combines the inherent porosity of connecting PLIC units at the nanoscale and the advantage of additive manufacturing at macroscopic scale that enables conventional powder-like porous materials be constructed to intricate designed architectures unattainable with conventional fabrication schemes.

The fundamental building block of the PLIC 3D printing resin is based on  $Zr_6O_4(OH)_4$  with 12 methacrylic acid (MAA) ligands (Figure 1A). The structure extends from prominent zirconium-based MOF (UiO-66), possessing attractive thermal and chemical stability with ultrahigh surface area. The methacrylic acid ligands serve two functions: first to provide colloidal stability and second as a molecular connector by photopolymerizing the carbon double bond.

As demonstrated below, we note that additional functionalities can be obtained by exchanging the surface-bound ligands after processing. The inherent compatibility with a broad spectrum of ligand chemistries makes this approach interesting for applications separation applications that rely on programmable interactions between the fluid and the functionalized surface of the particle.

To underscore the practical utility of the mesoporous structures that can be fabricated using the method, we demonstrate the proof-of-concept 3D printing of a highly porous artificial leaf. In nature, the structure of plant leaves has been refined through billion years of evolution to endow all levels of hierarchy from macropores for fluid and nutrient transportation, micropores for gas diffusion and nanopores for gas adsorption to perform complicated and optimal functionalities.

In light of the inherent multi-functionality enabled by the hierarchical porous superstructure of natural leaves, we 3D printed an artificial leaf as shown in Figure 2. We 3D printed the designed leaf with macroscale veins like channels in the middle layer, microscale stomata like pores only on the back surface and nanoscale spongy mesophyll cells like voids. Figure 2 indicates the printed features of both structure and functions in multilevel scale. The channels provide the similar function for mass transportation and the stomata is for gas diffusion. Furthermore, we employed the thio-ene chemistry to post synthesize the residual carbon double bond with

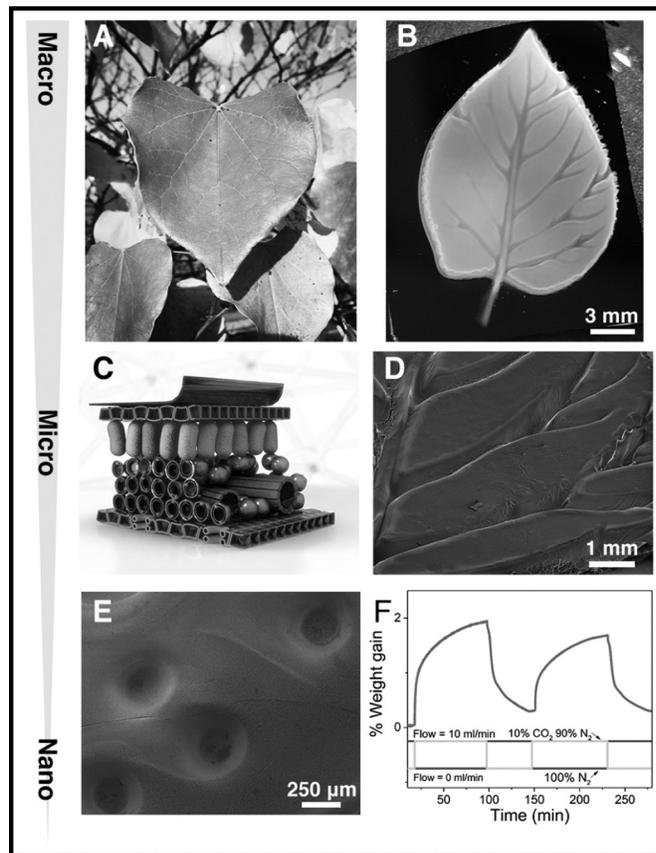


Figure 2: Complex devices like artificial leaf can be fabricated with 3D printing PLIC. (A) Photographic image of leaf. (B) Photographic image of artificial leaf. (C) 3D illustration of leaf structure from cross-sectional view. (D) SEM image of channels mimicking veins. (E) SEM image of small pores like stomata on the back surface (F) CO<sub>2</sub> capturing capacity of 3D printed artificial leaf. See full color version on pages xxviii-xxix.

cysteine ( $C_3H_7NO_2S$ ), anchoring the amine group into the nanoscale pores. To underscore ability of the artificial leaf to capture CO<sub>2</sub>, we exposed the leaf to 10% carbon dioxide 90% nitrogen under 30°C and 1 atmosphere. The nanoscale pores in artificial leaf show the ability to adsorb up to 1.92 weight% carbon dioxide per gram of the leaf.

The artificial leaf not only identifies the benchmark to build complex porous material-based devices but also opens pathways to research the benefits of biomimetic structures.