# Supplementary Materials for

# Three-dimensional printing of hierarchical porous architectures

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Table S1

Figs. S1 to S16

References

The current state-of-the-art in additive manufacturing nanoparticle related inks. Present 3D printing strategies involving nanoparticles have been demonstrated for different applications like conductive structures and ceramic (table S1). However, the lack of control at nanoscale impede the construction of complicated higher-order superstructures such as mesoporous material. Bridging the gap form fabricating nanoscale porous materials into 3D macroscopic architectures has presents a challenge with significant scientific and technological interest.

Main compositions	Strategy	Usage	Ref.
Zr <sub>6</sub> O <sub>4</sub> (OH) <sub>4</sub> -MAA PLIC	Printable nanocluster	Porous material	This work
SiO <sub>2</sub> nanopowder + monomer	Add nanopowder	Glass	1
$Ir_2O_3$ + monomer	Add nanopowder	Ferromagnetic structure	2
C <sub>6</sub> H <sub>14</sub> NiO <sub>21</sub> + monomer	Add metal containing solution	Metal	3
AgNO <sub>3</sub> + monomer	Add metal containing solution	Conductive structure	4
$Si(OC_2H_5)_4$ + monomer	Add inorganic solution	Hybrid material	5
Si containing monomer	Choose inorganic containing resin	Ceramic	6
Si containing powder + Si containing monomer	Add powder in inorganic containing resin	Ceramic	7
$Al_2O_3$ + monomer	Add powder	Hybrid material	8
Pt & Ir <sub>2</sub> O <sub>3</sub> nanoparticles + monomer	Load nanoparticles after printing	Micromachine	9

X-ray scattering structure analysis



Fig. S1 PXRD of  $Zr_6O_4(OH)_4$ -MAA PLIC before and after printing. The synthesized zirconium methacrylate oxocluster possesses feature peaks at 5.9° and 7.6° being consistent to the reported<sup>10</sup>. More information of the crystal structure could be found in the references<sup>11,12</sup>.

## **Additional HRTEM analysis**



## Fig. S2 STEM of 3D printed Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>-MAA.

The building units are conserved after the reaction and form highly porous materials. The red dot shows the scale of 2 nm as the comparison size with the building units.

### PLIC fusion mechanism

I Free radical polymerization (photopolymer)



II UV ligand stripping (nanoparticle based ink in lithography)



Fig. S3 Mechanisms for PLIC ink.

Figure S3 illustrates two possible mechanism by which PLIC ink is patterned during the processing. Mechanism I is a normal route to initiate and propagate the polymerization for photopolymer used in the 3D printer<sup>13</sup>. Mechanism II is a proposed route for nanoparticle-based photoresist used in lithography<sup>14</sup>; the second mechanism involves photoinitiated detachment of surface-bound ligands which change the solubility of nanoparticles. In fact, the PLIC idea combine both the photoinitiator from mechanism I and similar nanoparticles from mechanism II. To better understand which mechanism is dominant, we have done control experiments and analyzed the mass distribution of products printed using PLIC inks. First, we couldn't get printed structures without adding photoinitiator, which suggests that mechanism I is dominant. Second, GPC analysis suggests that there are no fragments with mass larger than 1000 Da, indicating no long polymer chain in the samples. Therefore, we propose that the mechanism I is the main mechanism but some ligands may drop from the nanoparticles and participate in the propagate reaction when projecting 2D UV patterns.

### **FTIR** analysis





(A) The three COO<sup>-</sup> vibrations and Zr-O vibration are highlighted, showing coordinated methacrylic acid to the Zr-oxide core<sup>15,16</sup>. Besides, the pattern is highly relevant to DAX #10773 zirconium methacrylate. (B) The decreasing peak around 1600 cm<sup>-1</sup> shows the consuming of C=C, which supports our proposed mechanism.

### NMR analysis



## Fig. S5 NMR of Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>-MAA PLIC.

The <sup>1</sup>H-NMR spectrum of synthesized building unit was measured using CDCl<sub>3</sub> as solvent. The signals match the reported spectrum of  $Zr_6O_4(OH)_4(methacrylate)_{12}^{12}$ . Signals at 6.14 and 5.55 ppm are from the methacrylate ligands. We couldn't observe OH signal which should be around 11.3 ppm.

**Dynamic Light Scattering (DLS)** 



Fig. S6 DLS of  $Zr_6O_4(OH)_4$ -MAA PLIC measured in toluene. The synthesized  $Zr_6O_4(OH)_4$ -MAA can be re-dispersed into proper solvent and form individual building units around 1.5 nm. The clusters stay stable in the solvent.

## PLIC resin solubility



## Fig. S7 Solvent comparison for ink formation.

 $Zr_6O_4(OH)_4$ -MAA crystal, solution of building units in PGMEA, benzene and cyclohexane are shown. For example, PGMEA and benzene are good solvents for the building units. However, building blocks are not soluble in solvent like cyclohexane, which makes assembly not printable.

### Photo-rheometer analysis



Fig. S8 Photo-rheometer for Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>-MAA ink.

The speed of the ink is measured by photo-rheometer. Gel point, the crossing point of storage module and loss module, is often used to calculate the minimum dosage needed to turn inks from liquid phase into solid phase. The ink shows the speed to print 750  $\mu$ m thick monoliths in 10 seconds.



### Processing structure relationships - the effect of ink solvent



Solvent chosen and processing are critical to conserve multi-level porous architectures. For example, shrinkage of the printed samples with direct drying make cracks in Fig. S8 (A). In addition, even the building units disperse well in the solvent like benzene, the printed samples exhibit more defects than using PGMEA as shown in Fig. S8 (B) with supercritical drying and (C) with freeze drying. Fig. S8 (D) to (F) demonstrates the surface area and pore-size distribution of Fig. S8 (C). The surface area decreases more than 50% compared with Fig. 3 (A). (Logo used with permission. University logotype above is trademarked by Cornell University, Ithaca, New York.)



#### Additional nitrogen sorption and surface area consistency

Fig. S10 BET consistency of different print speed and drying methods.

![](_page_12_Figure_0.jpeg)

Fig. S11 Porosity characterization of Fig. 4 sample.

(A) The nitrogen sorption and (B) BJH pore size distribution of 3D printed leaf in Fig. 4. The BET surface area is around 496 m<sup>2</sup>/g. The decrease of surface area may be caused by the filling of amine monomer or the degrade due to additional processing step. The pore size distribution is consistent to other samples.

## Thermal stability analysis

![](_page_13_Figure_1.jpeg)

## Fig. S12 TGA for thermal stability.

(A) TGA curves for printed sample with Zr-MAA PLIC ink. The significant weight loss starting from 400 °C is attributed to the decomposition of organic ligands, matching the loss to controlled PMAA. The printed sample (B) before and (C) after TGA analysis. The sample shrinks around 17% in length. (Logo used with permission. University logotype above is trademarked by Cornell University, Ithaca, New York.)

![](_page_13_Picture_4.jpeg)

### **Resolution of PLIC ink**

![](_page_13_Figure_6.jpeg)

The pattern of pixels from the light source could be observed in (A) from the overexposed sample. The brick-liked patterns possess the width around 40 µm being

relevant to the reported 50  $\mu$ m resolution. (B) A printed circle around 170  $\mu$ m with sharp edges shows the resolution is not affected too much by the PLIC ink.

![](_page_14_Figure_1.jpeg)

![](_page_14_Picture_2.jpeg)

![](_page_14_Figure_3.jpeg)

Comparison of polymerized methacrylic acid without PLIC were made. (A) shows the sample polymerized from 1 ml of methacrylic acid with 20 mg of PI. The sample is rigid and holdable. (B) and (C) show the sample polymerized from 63 mg of methacrylic acid (60% of 150 mg PLIC), 1 mg of photoinitiator in 1 ml of PGMEA by reacting for 5 mins before and after washing, respectively. The sample is relatively fragile and easily damaged compared with the samples from the PLIC ink (Fig. S13 A & B), supporting the nanocluster plays an important role in printing. (Logo used with permission. University logotype above is trademarked by Cornell University, Ithaca, New York.)

### **Degree of photopolymerization**

![](_page_15_Figure_1.jpeg)

Fig. S15 Photo-Differential Scanning Calorimetry (photo-DSC).

Degree of conversion is measured by photo-DSC to evaluate how many ligands in the Zr-MAA PLIC building blocks are reacted during the photopolymerization. The reaction heat, integral of the peak, was directly related to vinyl group consumed in the system by the following equation:

$$\alpha = \frac{\Delta H_t}{\Delta H_0}$$

where  $\Delta H_t$  is the reaction heat evolved at time t and  $\Delta H_0$  is the heat for complete conversion<sup>17</sup>. First, the  $\Delta H_0$  of methacrylic acid is measured and consistent to reported number<sup>18</sup>. The  $\alpha$  of Zr-MAA PLIC is 0.28 supporting around 28.3% of ligands are consumed during the 3D printing process. (Note: the unit in the figure is mW/mg of Zr-MAA, so the integral area is multiplied by 1.67 to include that only 60 wt% is methacrylic acid in the building block for the calculation of  $\alpha$ .)

### **3D** printing models

![](_page_16_Picture_1.jpeg)

Fig. S16 CAD model of artificial leaf.

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