Three-Dimensional Printing with Silica Cages

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Abstract:

Material scientists have now developed an extensive library of nano-sized building blocks, offering a vast panel of properties (optic, magnetic, plasmonic, catalytic, etc.). Nevertheless, combining these building blocks for the realization of multifunctional materials while controlling their structure from the nano- to the micro-and all the way to the macroscale still remains an open challenge in order to fully exploit their potential. In parallel, new material processing techniques such as 3D printing technologies are emerging for the fabrication of macroscopic highly engineered parts and devices. In this work, newly discovered silica nanocages are combined with digital light processing 3D printing technique for the rapid fabrication of mesoporous parts with arbitrary shapes and tunable internal structures. Complementary strategies are then deployed for the implementation and deliberate positioning of various functionalities throughout 3D printed objects with high control on the microstructure and macroscopic architecture of the superstructures. This approach paves the road for innovative device concepts and designs, that will benefit from the unique properties of nanomaterials and from the micro-and macroscale manufacturing capability of 3D printers.

Summary of Research:

In this work, the silica cages were made compatible with digital light processing 3D printing, through their functionalization with methyl methacrylate groups (Figure 1). In a previous study, calculations suggested that as part of their formation mechanism, the cages vertices and struts deform the surface of the micelles, with positively charged surfactant molecules wrapping the negatively charged inner surface of the cages. As illustrated in the inset of Figure 1a, this soft-template approach allows to distinguish the inner and outer surfaces of the cages, forcing the functional group to attach predominantly on the outer surface. Later in the synthesis process, the surfactant micelles were removed from the inside of the cages by dialysis in an acidic ethanol solution, causing the cages to precipitate in aqueous solution.
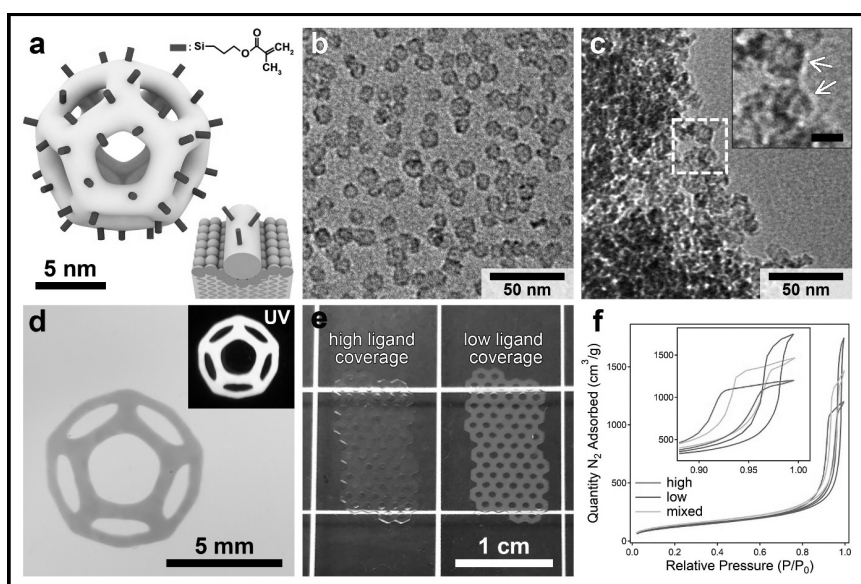

Figure 1: Illustration (a) and TEM image (b) of silica cages functionalized with methyl methacrylate groups (inset in a: illustration of a cage strut before removal of the surfactant micelle, in blue). (c) TEM image of a piece of a printed part (inset: zoom in, white arrows point to clearly visible cage structures, scale bar 10 nm). (d) Photography of a pattern printed on a glass substrate with dye functionalized cages (inset: photography under UV irradiation). (e) Photography of parts printed with silica cages with high (left) and low (right) methyl methacrylate surface coverage. (f) Nitrogen sorption isotherms of parts printed with high and low methyl methacrylate coverage, and with mixed samples (inset: zoom in the hysteresis range). (Find full color on pages xiv-xv.)

Although the original silica cage synthesis was upscaled 30 times in order to make the printing of large parts affordable, the transmission electron microscope (TEM) image in Figure 1b shows that cage structures were obtained with this modified method.

In Figure 1e, larger and free-standing parts exhibiting a honeycomb structure were printed with different ligand coverages and dried with Leica critical point dryer in CNF. For the part with low ligand coverage, the cages were functionalized with 2.5 times less than for the high ligand coverage. Although these two parts have the same dimensions, the low coverage one is 1.7 times lighter than the high coverage one. This important difference in density suggests different internal microstructures. These parts have relatively similar specific surface area, specifically 438 m^2g^{-1} and 450 m^2g^{-1} for the high and low coverage parts respectively, as determined by the Brunauer-Emmett-Teller (BET) method. Nevertheless, the hysteresis of the nitrogen sorption measurements (Figure 1f) show important difference in adsorption-desorption behavior.

The broader hysteresis of the high coverage part suggests that mesopores access is more restricted in this case, whereas in the low coverage part the mesopores access is facilitated by the presence of large pores and channels. This is also supported by the direct visual inspection of these parts (Figure 1e). While the high coverage part appears relatively transparent, the low coverage one is more translucent due to light scattering by larger pores. To induce significant Mie scattering, these larger pores should be at least few tens of nanometers in size and can only correspond to interparticle pores because the intraparticle pores, i.e. core of the cages, are less than 10 nm. Since the parts have similar specific surface area regardless of the ligand coverage, these large interparticle pores do not contribute significantly to the total surface area.

Instead, this property mostly derives from the intra-particle pores of the cage structures and from the microporosity of silica itself. Thus, varying the ligand coverage of cage-based PLIC inks is a powerful tool to purposefully tune the porosity and internal structure of 3D printed objects. Additionally, a PLIC ink was prepared by mixing the two cage samples in equivalent proportion. The isotherms of the resulting printed part, denoted as 'mixed' (Figure 1f), shows an intermediate behavior between those obtained with either purely high or low coverage, hence offering an additional knob to tune the microstructure of these macroscopic objects.

As an interesting feature, these parts can also be calcined in order to remove the organic component, yet fully preserving their fine microstructure.