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, silica cages were made compatible with digital light processing 3D printing, through our reported photoresponsive ligand on inorganic core (PLIC) concept [1].

Making use of the printed cage-based mesoporous materials, we developed a hitherto unknown internal 3D printing approach. Here, the porosity of an already printed 3D part serves as a scaffold for the subsequent printing of a second 3D material directly within the first. To demonstrate this concept, we printed a second metal structure within the pores of the first silica structure. As illustrated in Figure 1, a 3D block of silica cages was first printed as described before and then soaked for 30 minutes in a solution of silver nitrate (0.1 M in 10:1 v/v ethanol:toluene), and two photoinitiators, namely TPO (0.05 M) and Darocur 1173 (0.5 M). In this case, TPO acts as a sensitizer for Darocur 1173, which serves as the electron donor for the reduction of Ag^{+} to Ag^{0}.

A light pattern was then projected in the form of three lines to locally reduce silver, which remained embedded in the original 3D silica block (Figure 1d-f). The 3D printing of a second, more active material within a 3D printed mesoporous silica block opens a whole new scope of opportunities. Through this approach, the two materials are entangled with each other, which means that the structure of the scaffold or host material will influence the structure and therefore properties of the guest material.

As an example, deliberately varying the porosity of the silica host could allow to tune the electrical conductivity along the metal lines. Furthermore, the entanglement of the two materials also means that interactions between them such as charge transport, are possible and may even benefit from their high interfacial area. This approach can readily be extended to a large variety of materials offering a wealth of unique properties.

For instance, printing two different catalytic materials within a porous silica scaffold could result in a highly tunable platform with controlled symmetry and flux for tandem catalysis applications. The whole 3D printing toolbox can thereafter be put to practice for the positioning of active centers within the host scaffold with a great degree of freedom.

References:

[1] Huang, J.-Y. et al. Three-Dimensional Printing of Hierarchical Porous Architectures. Chem. Mater. acs.chemmater.9b02761, doi:10.1021/acs.chemmater.9b02761 (2019).

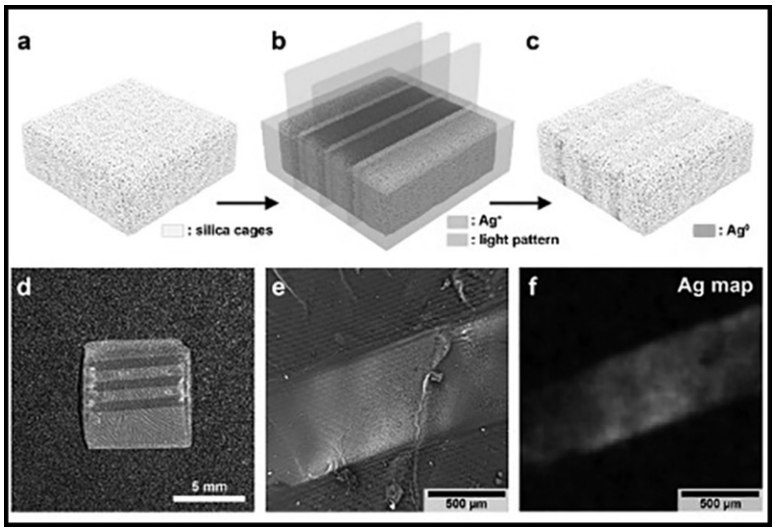

Figure 1: a-c, Illustration of the process of printing silver within a primary part printed with porous silica cages. First, a block of silica cages without additional functionalization is printed (a). The block is immersed in a solution of silver nitrate and photoinitiators. A light pattern in the shape of lines is then projected onto this block (b), resulting in the localized reduction of Ag^+ ions into Ag^0 (c). d, Photograph of the resulting block of silica cages exhibiting three lines of metallic silver. Backscattered electron-based SEM image (e) and EDS map (f) of a silver line embedded in the porous silica matrix.