Micro- and Mesoporous Silica and Titania for Catalysis, Biomedizin, Photonics

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Abstract
A combination of laser-based 3D structuring and chemical bottom-up processes to prepare hierarchical pore structures is presented. Polymer templates with dimensions in the micrometer regime are fabricated by two-photon polymerization and are subsequently infiltrated with mesostructured silica and titania. Calcination to remove both, the macro-templating polymer and the nano-templating surfactant molecules, has been carried out, delivering mesoporous constructs which correspond to an inverse replica of the initial polymer structure. As the two-photon polymerization allows controlled construction of various shapes, mesoporous materials can be constructed with practically any desired morphology on the micrometer scale. The dual pore system of macro- and mesopores classifies these materials as hierarchical pore systems with applications in catalysis and sorption. In addition, the versatility of silica and titania surface chemistry opens new venues for the fabrication of photonic crystals. The general biocompatibility of silica and titania further allows the construction of scaffolds for biomedical applications.

Article
Femtosecond laser technology is nowadays widely used for the realization of three-dimensional (3D) micro- and nanostructured materials. Nonlinear polymerization processes allow the fabrication of 3D microoptical and micromechanical devices [1,2] as well as photonic crystals and photonic crystal templates [3]. This photo-fabrication process is accomplished by 2-photon absorption of visible or near-infrared femtosecond laser pulses from ultrashort pulse laser systems. The two-photon polymerization (2PP) technique allows the fabrication within the volume of the photosensitive resins. When femtosecond laser pulses are tightly focused into the volume of a photosensitive material (or photoresist), 3D structures with resolution below 100 nm have already been realized [4]. This gives the possibility for the fabrication of any computer-generated 3D microstructure by direct laser-"writing" into the volume of a photosensitive material and especially for the realization of specially designed microporous media (see Fig. 1) for chemical, biomedical, and photonic applications.

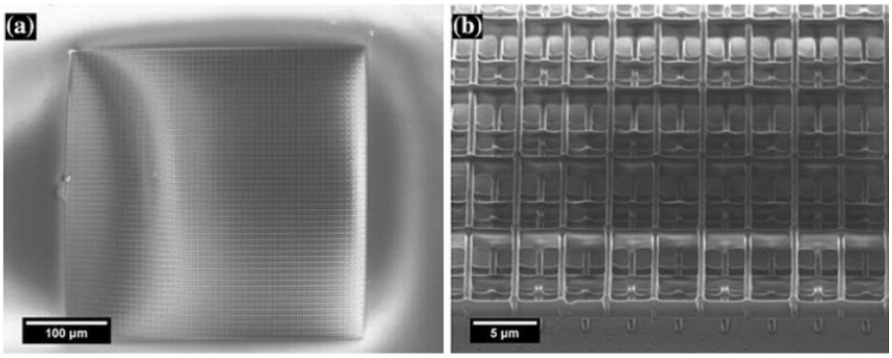

Fig. 1: 3D woodpile temples fabricated by 2PP. a) A four layer 350 µm x 350 woodpile polymer crystal. b) Magnfied image showing sub-µm polymer rods

On the other hand, the class of ordered mesoporous silicas has widely been investigated since such materials were first presented by the Mobil Oil Co., in 1992 [5,6]. Reasons for this interest are the large surface areas of these ordered mesoporous silicas and their applications in sorption processes and catalysis. Besides the development of different mesoporous bulk materials like MCM-41 or SBA-15, there was an early and profound interest to obtain ordered mesoporous silicas as a film on a substrate for use in biomedical devices [5].

Here, the realization of hierarchical micro- and nanopores structures in mesoporous silica and titania is described. The scheme of the strategy for the construction of these replicas is shown in Fig. 2. In short, after the preparation of a template by 2PP of a suitable polymer, the sample is coated by a layer of ordered mesostructured silica or titania from which the organic substances are finally removed by calcinations to yield materials hierarchically structured on the micrometer and on the nanometer scale.

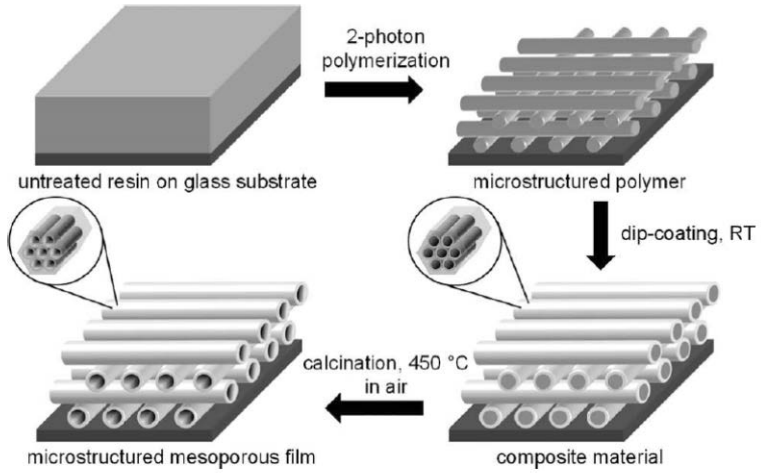

Fig. 2: Synthetic strategy for the combination of 2-photon polymerization and formation of mesoporous coatings.

The possibility to combine sub-µm top–down construction with the bottom-up self-assembly of nm-structured materials gives rise to a variety of applications. Such materials are of considerable interest in chemistry, as the system of large pores can facilitate transport to the smaller pores where sorption or catalytic reactions can take place.

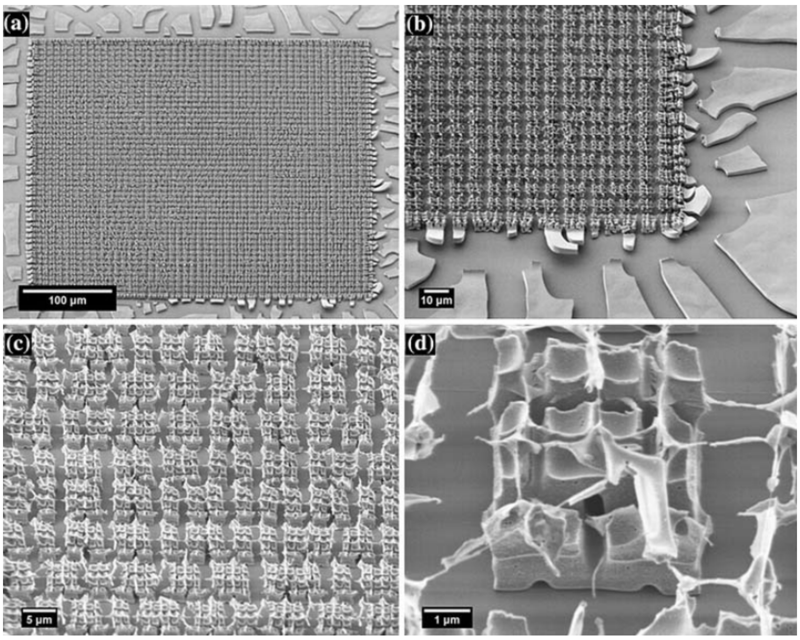

Fig. 3: SEM images at different magnifications of a inverse woodpile structure in mesostructured titania.

Such catalytic converters and chemical adsorbers based on hierarchical structures might thus find wide ranges of applications in industrial emission control and automotive industry. For applications as biomaterials, large pores of hierarchically ordered porous materials could allow for the ingrowth of cells into a scaffold material, while the storage capacity of the mesopores can deliver signalling molecules, drugs or nutrients. The construction of specified 3D structures is also of interest for the realization of photonic crystals providing 3D stop bands. To realize photonic crystals with a full photonic bandgap, 3D structuring of high refractive index materials is required. An example of a realized inverse woodpile titania structure is shown in Fig. 3. It has been shown that after calcination the amorphous titania has been transformed into crystalline anatase. Noteworthy, the refractive index of anatase of 2.6 and is thus large enough for opening complete optical band gaps [6].

The results presented here show novel possibilities to combine the laser-based top-down approach of structuring materials on the micrometer scale by 2PP with a chemical bottom-up self-organization process for producing artificial hierarchically ordered porous media for applications in chemistry, biomedicine, and photonics.

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