

Random laser device: hierarchical porous silica monoliths obtained from silk fibroin as biotemplate

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In nature, biopolymers have been applied as control agents or as templates of the inorganic precipitation and crystallization. Besides, they also may be assembled and form structures that serve to confine spaces or serve as scaffolds for the formation of the inorganic component. From the materials science perspective, the biopolymers can be versatile source for the design of structured inorganic materials in the laboratory. Among all natural polymers, silk fibroin extracted from *Bombyx mori* silkworm cocoons offer unlimited opportunities for functionalization, processing, and biological integration. Regenerated fibroin solution can be processed to form a variety of materials such as hydrogels, ultrathin and thick films, 3D porous matrices and fibers with controllable diameters¹. Considering the advantage of the relationship between structure and processing of the silk fibroin in this work it was designed structured organic-inorganic hybrids (OIH) based on silica and silk fibroin. The designed materials were obtained as robust monoliths containing different fibroin fractions. The SEM images demonstrated *in situ* self-assembly of fibroin nanofibers dispersed into the IOH monoliths. Structural characterization of the OIH monoliths was performed by Raman and solid state NMR spectroscopies. Our findings demonstrated that fibroin nanofibers have prevailing β -sheet conformation. The results shows that the transition of amorphous to crystalline state was favored by increase the fibroin fractions in the samples. In addition, we demonstrated that these materials can be used to prepare porous silica monoliths for random laser applications. The mesoporous and microporous silica monoliths template were obtained using fibroin nanofibers as sacrificial scaffolds through selective removal via heat treatment of IOH. The porous silica monoliths doped with rhodamine 6g (Rh6G) exhibited efficient RL action with low threshold power excitation and narrowing linewidth². Minimum laser threshold of 9.7 μ J/pulse and a linewidth narrowing from 40 to 4 nm were observed. The silica monoliths based RL operates in the incoherent feedback regime and can be potentially used for speckle free laser imaging. In addition, analysis of the emission spectra showed two gain mechanisms coupled, the random lasing and the stimulated Raman scattering, allowing us to observe a Stokes line of the dye. This behavior was recently reported in the literature³ and it has been observed in others porous materials.

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3. Hokr, B. H. *et al.* Random Raman lasing. **Nature communications**, v. 5, 2014.