Directing the microstructure and shape morphosis in the self-assembled silk fibroin biopolymer hybrids as advanced multifunctional aerogels

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Silk fibroin (SF) is a multifunctional naturally occurring biopolymer that presented various illustrious properties like biocompatibility, biodegradability, and versatile processability. Recent SF aerogel *so-called AeroSF*, developed by Maleki *et al.* [1] and it's composite prepared by *in-situ* self-assembly of SF with various organosilanes [2] comprised several interesting physical properties such as high surface area, ultra-low density, and ultra-low thermal conductivity. Nevertheless, improvement in the number of properties and controlled microstructure, macroscopic shape, printability, reversible flexibility, and thermal resistance are still required to render SF based aerogel counterparts highly promising for some advanced applications. Thus, in our current study, we take advantage of a synergistic combination of surface chemistry modification, self-assembly, sol-gel, together with 3D printing and directional freeze casting techniques [3], and managed to develop various highly porous 3D monoliths, beads and printed constructs with multiple shapes and controlled anisotropic microstructures (*cf*. Fig. 1) .

Namely, we developed biomimetic highly flexible SF-MXene aerogel hybrids that indicate reversible compressibility, nacre mimetic brick-mortar underlying microstructure, and ultra-low density. We proposed the developed monoliths for several high-performance applications, mainly as flexible pressure sensor devices. Additionally, the antibacterial and highly cell responsive 3D printed aerogel construct has been developed by self-assembled and surface modified silk fibroin-silica hybrid hydrogels as ink. After the freeze casting and freeze-drying process of printed constructs, the aerogel implants become a competent antifouling and bone regenerative implants for bone tissue engineering. What' s more, we are also currently developing highly porous and intriguing millimetric and micrometric sized core-shell beads through cryo-assembly, and cryo-assembly assisted electro-spraying of surface-modified SF. The designed beads presented a high affinity toward reversible adsorption-desorption of Cu(II) ions, organic dyes, and solvents from aqueous media.

In brief, We demonstrated that a combination of surface-modified SF biopolymer, self-assembly, and sol-gel, together with directional freeze casting and 3D printing technology, could be synergistically exploited to develop 3D porous structures with intriguing properties.

[1] H. Maleki**et al.*, ACS Appl. Mater. Interfaces 2018, 26, 22718-22730.

[2] [a]H. Maleki* *et al.*, J. Mater. Chem. A, 2018, 6, 12598–12612. [b]H. Maleki* *et al.*, ACS Appl. Mater. Interfaces, 2019, 11, 19, 17256–17269.

[3] H. Maleki* et al. Adv. Eng. Mat, 2020, DOI: 10.1002/adem.202000033.

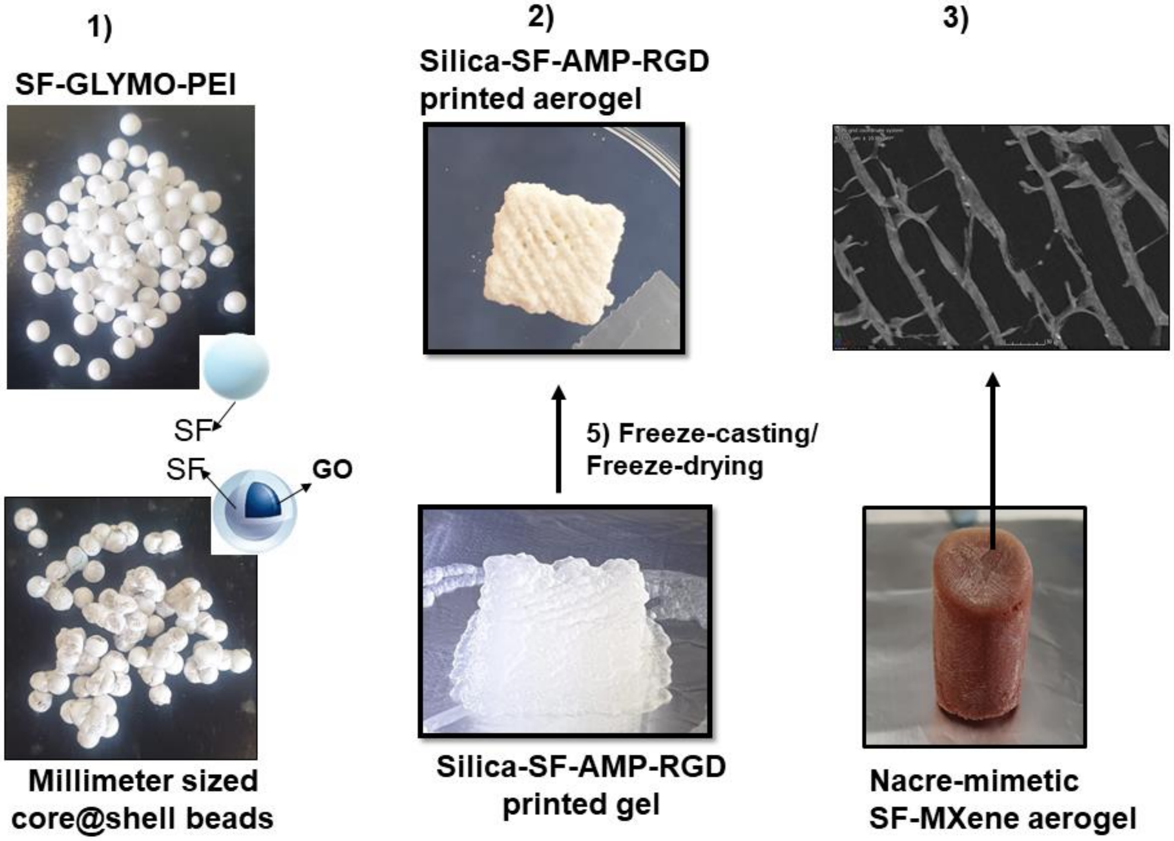
1)
SF-GLYMO-PEI
SF
SF
GO
Millimeter sized
core@shell beads
2)
Silica-SF-AMP-RGD
printed aerogel
5) Freeze-casting/
Freeze-drying
Silica-SF-AMP-RGD
printed gel
3)
Nacre-mimetic
SF-MXene aerogel

Fig. 1