Hierarchically organized biomimetic architectured porous silk fibroin based anisotropic aerogels for thermal energy management

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Given the urgent requirement for energy-saving, the research on thermally super-insulating and mechanically flexible materials with the ability of thermal energy management is becoming vitally important. In this regard, the fabrication of bioinspired anisotropic aerogels has recently drawn high interests[1]. While traditional super-insulating silica and biopolymer aerogels have vastly been developed in recent years, their low mechanical strength, poor fire-resistance, and high moisture sensitivity are still major challenges to mitigate. Also, most of the aerogels reported hitherto are microstructurally isotropic, which is not sufficient for thermal energy management. Silk fibroin (SF) is a biopolymer extracted from *b. Mori* silkworm cocoon, which has been used for the processing of various intriguing functional materials[2]. The application of the SF based biopolymer for developing various functional aerogels based thermal insulators is quite a new trend that has been very recently started by Dr. Maleki for the first time[2,3]. In this project, we structurally designed a series of anisotropic SF based aerogel composites through a robust green approach. This includes 1) silylation of SF biopolymer using silane chemistry, 2) cross-linking of silylated SF with glutaraldehyde (GA) as an organic cross-linker (SF-GA), and 3) co-self-assembly of the resulted SF-GA with various ceramics, *e.g.,* nanostructured silica, 2D titanium carbide (Ti_3C_2OH, MXenes) nanosheets, Sepiolite ($Mg_2H_2Si_3O_9.xH_2O$) nanorods as the secondary inorganic phases to develop composite gels. The developed self-assembled hybrid gels were undergone to the bioinspired processing of directional freeze-casting and freeze-drying to afford lightweight, mechanically robust, thermally insulating and fire-retardant hybrid aerogels. The incorporation of secondary inorganic phases to SF gels is particularly very appealing as they not only significantly reduce the solid heat conduction because of their phonon scattering but also conferred a fire-retardant effect to the designed final aerogels' composites. Also, the developed hybrid aerogels have indicated a multiscale anisotropy in their microstructure ranging from hierarchical organized, aligned lamella to nacre-mimetic brick-mortar structures, interesting for energy management strategies.

1. B. Wicklein *et al.,* Nat. Nanotech, 2015, 10, 277–283.

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

3. H. Maleki *et al.,* J. Mater. Chem. A, 2018, 6, 12598–12612.