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Communication

A Novel Facile and Green Synthesis Protocol to Prepare High Strength Regenerated Silk Fibroin/SiO_2 Composite Fiber

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Abstract: In this work, regenerated silk fibroin (RSF) and silicon dioxide (SiO_2) composite fiber was successfully extruded by wet spinning method. The effect of SiO_2 addition on structure of the composite fiber at microscopic level is studied, which subsequently correlated to the mechanical performance. The best concentration ratio for composite fiber is identified by screening SiO_2 concentration from 0.025 w/w% to 0.5 w/w%. The experimental results revealed that the SiO_2 at a low concentration of 0.1 w/w% was well distributed. The breaking stress, breaking strain and Young's modulus at 0.1 w/w% SiO_2 addition of the RSF fibers increased considerably compared to the neat RSF fibers from 243±3 to 458±21 MPa, 51±4 % to 54±7 % and 6.34±0.55 to 11.69±1.12 GPa, respectively. To the best of our knowledge, this is the first report for RSF/SiO_2 composite fiber. We believed the insight provided in this report which looks into the structural evolution should be beneficial to the future design and building of other advanced functional fibers.

Keywords: Fibre technology, Wet spinning, Regenerated silk fibroin, SiO_2, Mechanical performance

Introduction

Biomaterial from nature plays an essential role since ancient era in making mankind comfort. Owing to the extraordinary features, such as the good mechanical strength, moderate elongation, biocompatible and nonhazardous properties, natural silkworm cocoon silk has been widely applied in diversified fields including textile, biomedical and biotechnological industries [1-3]. However, the mechanical strength from naturally obtained silk fiber is still limited, which consequently to a large extent restricts their applications towards futuristic uses. In this regard, the exploration of new synthesis protocol for manipulating properties of artificial silk fibers is one of the key concerns of current research. Previously, it is reported that by incorporating some specific fillers into the RSF composite fibers, the mechanical properties can be improved accordingly. For instance, these fillers refer to the keratin [4], graphene and graphene oxide [5]. Although these fillers are capable to improve the breaking stress, they still fail to improve the extensibility of the RSF fibers. On the other hand, these additives are also so expensive that they can only meet for research purposes.

Silicon oxide (SiO_2), one of the most popular inorganic material has claimed mechanically strong, thermally stable, chemically stable and high durable in hot water [6]. Consequently, SiO_2 have been reported to prepare composite materials that can show higher stability [7].

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In this work, the composite fiber composed of the RSF nanofibrils and SiO_2 particles is prepared by easy and green wet spinning method [8]. The best concentration ratio for composite fiber is identified by screening SiO_2 concentration from 0.025 w/w% to 0.5 w/w%. The structural characteristics of the composite fibers were investigated thoroughly. It is clearly indicated that the mechanical performance should be highly correlated to the microscopic structures. Specifically, the percentage of β-crystallite can directly have impact on mechanical properties such as breaking stress and Young's modulus [9]. In summary, our obtained results showed that the addition of SiO_2 provides heterogeneous nucleation sites to initiates β-crystallite formation and eventually give rise to the improvement of mechanical performance. Addition of SiO_2 particles as a filler reveals positive impact to improve both the mechanical stress and strain of the composite RSF fiber, which is considerably higher compared to the neat RSF fibers. The acquired results should provide insights into the structural evolution within the composite fiber, which would be beneficial to the future design and building of high-performing fibers.

Experimental

Material and Method

In exception to natural silkworm cocoons, the rest of chemicals are of analytical grade and used as received without further purification. *Bombyx mori* silkworm cocoons were provided by Guangxi Sericulture Technology Co., Ltd. (Guangxi, China). Silicon dioxide nanoparticles (SiO_2 NPs)

(average diameter of 20 nm and 220 nm) were procured from Guangzhou Suixin Chemical Co., Ltd. (Guangzhou, China).

Wet Spinning of RSF/SiO_2 Composite Fiber

RSF solution with different ratios of SiO_2 nanoparticles (NPs) was transferred to a 5 m*l* syringe at room temperature. A high-pressure injection pump (LSP01-1BH, Baoding Longer pump) was used to extrude the RSF solution through a 27 gauge needle whose inside diameter is 210 μm at a speed of 10 μ*l*/min, directly into an aqueous 35 % (w/v) $(NH_4)_2SO_4$ coagulant solution at room temperature. The fibers were wound out of the coagulation bath through four rollers of 4 cm diameter at 12, 24, 36 and 48 rpm respectively, with subsequent steam annealing to enhance the crystallinity [10]. In the final, composite RSF fibers were obtained. The details of experimental characterization have discussed in the supporting information.

Results and Discussion

Figure 1 represents schematic illustration of the synthesis protocol of RSF/SiO_2 composite fiber. In order to fabricate a composite fiber with high tensile properties, mixing parameters were optimized by varying SiO_2 concentration, from 0.025 w/w% to 0.5 w/w%. The detailed synthesis protocol, instrumental information and characterization details are incorporated in supporting information.

The morphology of all composite fibers at different SiO_2 concentration shows a smooth surface, which is the same as the neat RSF fibers (Figure 2(a), Figure S1), and no apparent SiO_2 aggregates were noticed by the SEM image, suggesting a homogeneous dispersion of SiO_2 in the RSF matrix [11]. To identify the location of the SiO_2 NPs, energy dispersive X-ray mapping (Figure 2(b)) and Energy dispersive spectrometer (EDS) were also applied on the composite fibers (Figure 2(c)). XPS measurement was used to investigate chemical composition of as prepared composite fiber (Figure 2(d)), confirming the presence of C, O, N, and Si. The doping of SiO_2 in composite fiber was also confirmed by FTIR spectrum, wherein additional peak at 1104 cm^{-1} is indication of -Si-O- bonding (Figure 2(e)). The XRD results of the SiO_2, RSF and RSF/SiO_2 composite fibers are shown in Figure 2(f), while no diffraction peak from SiO_2 was observed signifies molecular level dispersion of SiO_2 in composite.

In general, the mechanical performance of composite fiber is correlated to the percentage of β-crystallite [12]. In this concern, percentage of β-crystallites were investigated and correlated to the mechanical properties of the RSF/SiO_2 composite fibers prepared by varying concentration of SiO_2 from 0.025 w/w% to 0.5 w/w% (Figure 3). Figure 3(a) and Table S1, comprises the data acquired using FTIR and SAXS showing percentage of β-sheet and β-crystallite (Figure S2 and Figure S3). The mechanical performance of composite fibers was also given in Figure 3(b) and Table S1. Wherein, RSF/SiO_2 composite fibers showed improved mechanical performance than that of the degummed silk fiber (DSF) and pure RSF fibers (Figure 3(c) and 3(d)). Up to 0.1 % addition of SiO_2 the similar trend was recorded in mechanical performance, whereas above 0.1 % the mechanical properties of composite fibers decreased. The breaking stress, breaking strain and Young's modulus at 0.1 w/w% SiO_2 addition increased considerably compared to the RSF

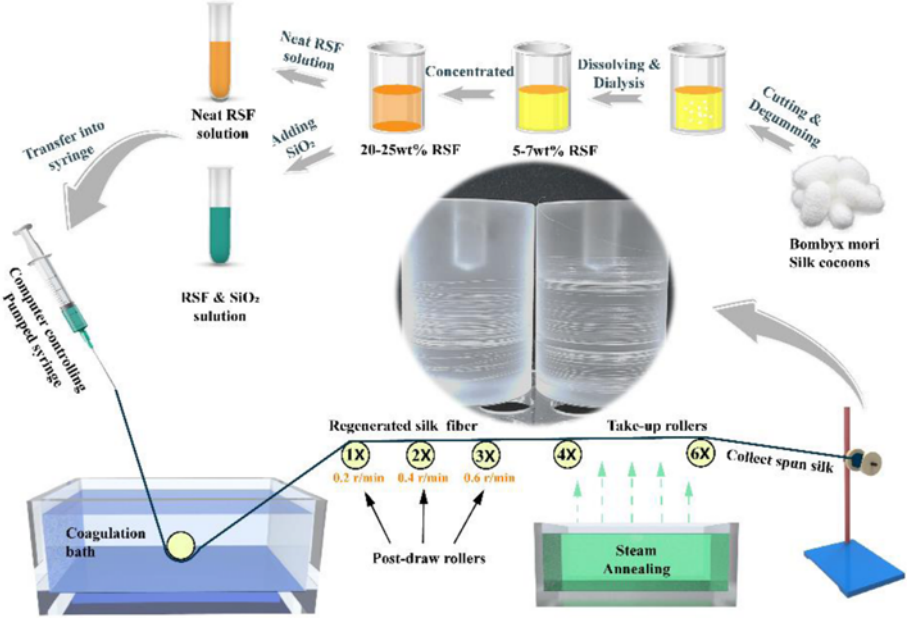

Figure 1. Schematic illustration showing synthesis protocol of RSF/SiO_2 composite fiber.

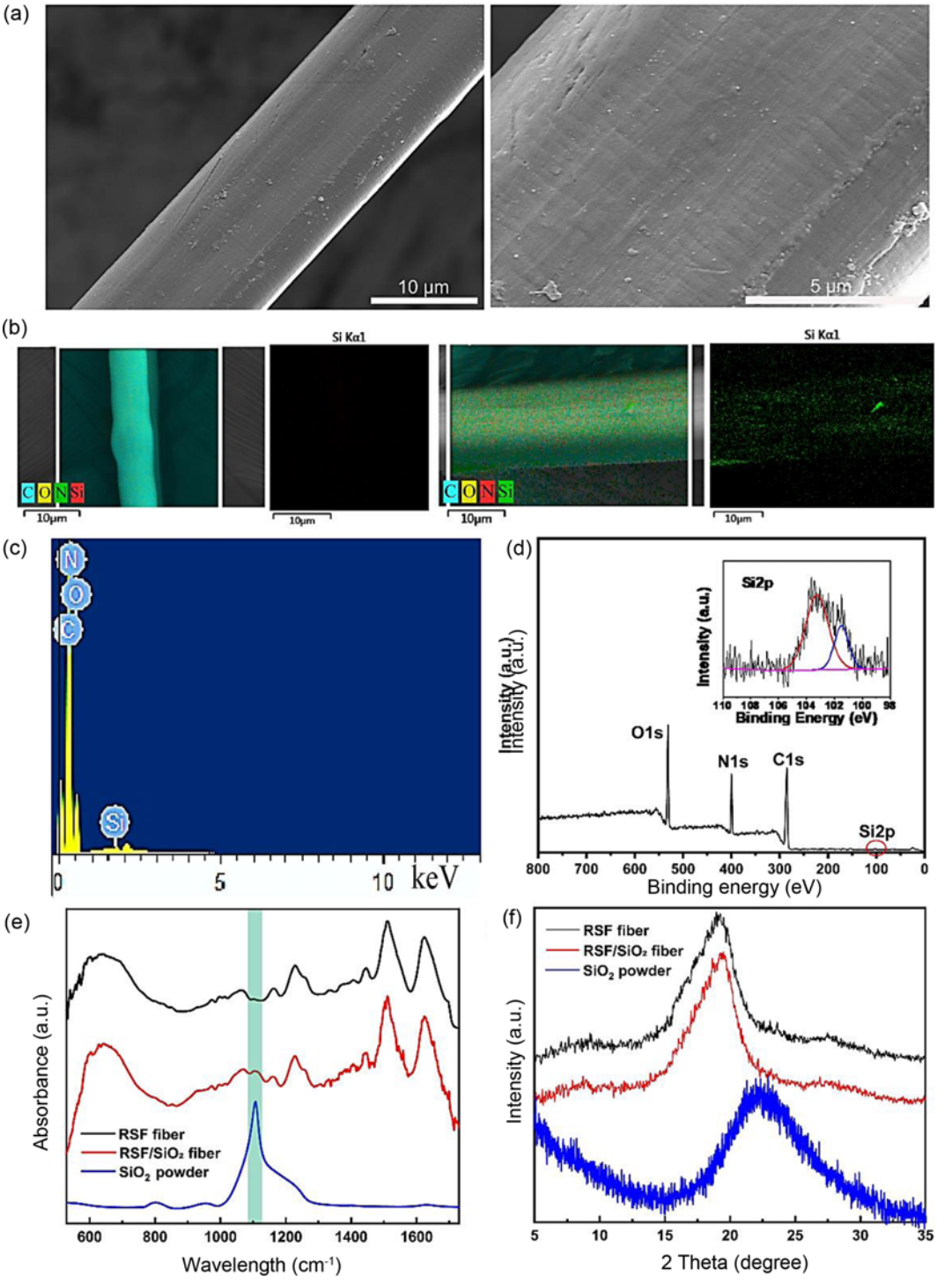

Figure 2. (a) SEM images of wet-spun RSF(left) and RSF/SiO_2(0.1 w/w%) fiber(right), (b) corresponding elemental mapping, (c) EDS elemental analysis, (d) survey XPS analysis, XPS core level spectra of Si2p (inset), (e) FTIR spectra of RSF, RSF/SiO_2 and SiO_2, and (f) the XRD patterns of RSF, RSF/SiO_2 and SiO_2.

from 243±3 to 458±21 MPa, 51±4 % to 54±7 % and 6.34±0.55 to 11.69±1.12 GPa, respectively (Table S1). In addition, effect of filler size is also investigated, wherein SiO_2 of 220 nm is used to prepare RSF/SiO_2 composite fiber (Figure S4). The obtained results showed improved mechanical performance as compared to neat RSF but less than RSF/

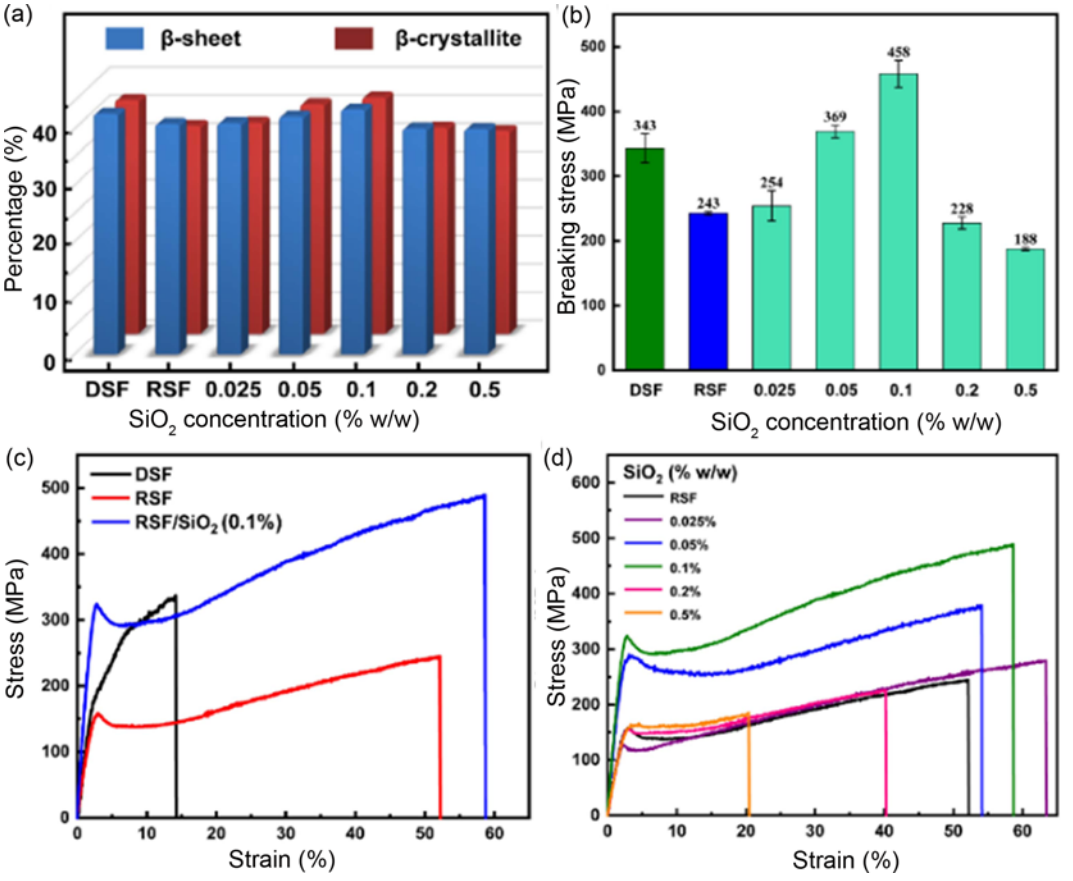

Figure 3. (a) β-sheet and β-crystallite percentage of DSF, RSF and RSF/SiO_2 fiber, (b) breaking stress results of DSF, RSF and RSF/SiO_2, (c) experimental results showing Stress-strain performance of DSF, RSF and RSF/SiO_2, and (d) experimental results showing Stress/-strain performance of RSF/SiO_2 composite fiber with the concentration of SiO_2.

SiO_2(20 nm) composite fiber. In principle, the addition of SiO_2 provides heterogeneous nucleation sites to SF silk fibroin molecules so that they promote the β-crystallite crystallization [9]. On the other hand, it is also noticed that when the ratio of SiO_2 is above the critical value, i.e., 0.1 w/w%, the content of both β-sheet and β-crystallite in RSF fibers would decrease, which can be explained by the phase separation theory [13], in which those fillers tend to aggregate and more be more likely serving as some "defects" so that they may subsequently give rise to an inferior mechanical performance. The recorded Young's modulus for our prepared RSF/SiO_2 composite fiber is much higher in comparison to the available literature reports using hydroxyapatite and functionalized graphene oxide (FGO) as the fillers [5,14].

Conclusion

In summary, we have prepared the RSF/SiO_2 composite fiber by a simple and eco-friendly wet spinning technique. The distribution of SiO_2 and structure of composite fiber are investigated by sophisticated analytical techniques. The prepared composite fibers display the high breaking stress, breaking strain and Young's modulus, which is 458±21 MPa, 54±7 % and 11.69±1.12 GPa, respectively. The results indicate that the SiO_2 in composite fiber help to bare external load. According to the available literature and our understanding, this is the first report wherein SiO_2 serve as a filler material to fabricate mechanically enhanced composite silk fibers.

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