From spider webs to a fibre-optic chemical sensor

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From the spider's perspective, silk is not only a building material but also a safety net, a weapon and a sensory organ to detect the presence of prey on its web. For scientists, dragline silk - directly extracted from spiders - is a tough, biodegradable and biocompatible optical fibre. These protein optical threads are made up of millions of repetitive protein sequences and domains that, unlike its silica counterpart, can interact with a multitude of chemical species. In this communication, we will explore the potential of using spider silk as a new type of fibre-optic chemical sensor.

Introduction

A spider can spin up to seven different types of silk (Fig. 1), which all have a specific function in the web: for example viscid silk is used by the spider to catch preys while dragline silk serves as material for the framework of the web. The latter is reputed for its high tensile strength and extreme toughness [2], which is exploited to make strong and extendible textile fibres. Combining their biocompatible nature to these extraordinary mechanical properties, they are also the perfect candidates for medical applications such as tissue engineering [3]. Amazingly, these silk wires can also be used as photons carriers and recently, light guiding along a dragline silk was demonstrated with transmission losses of the order of a few dB/cm [4-6], which paves the way for their use as a biological optical fibre in living organisms. In this work, we will show how these protein-based threads can also be used as a new generation of optical fibres for chemical sensing.

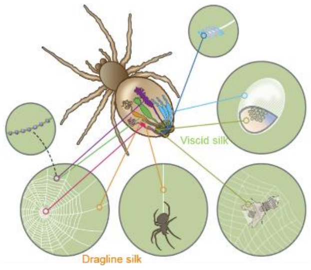
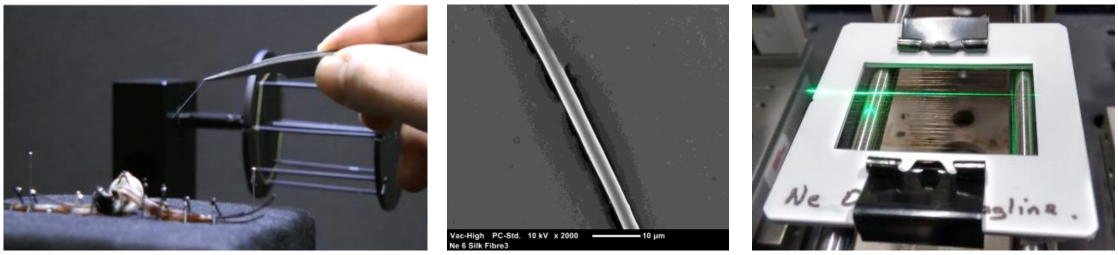


Fig. 1. Different types of silk produced by the spider for different functions in the web [1].

Dragline silk used as an optical fibre

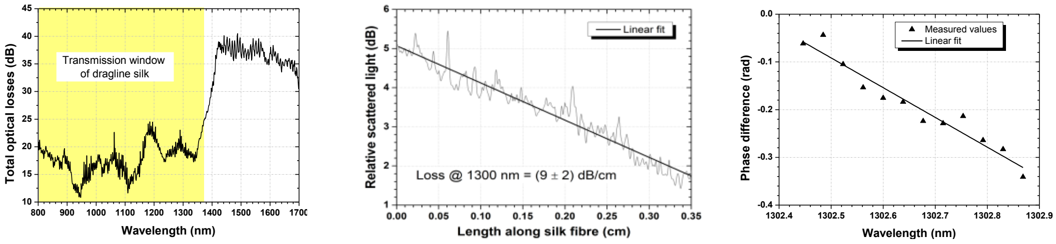
For our experiment, we used dragline silk directly collected from the major ampullate gland of a female *Nephilia edulis* spider (Fig. 2a). The reeling process, performed by the Oxford Silk group under controlled conditions, resulted in a uniformly spun fibre with a smooth surface, circular cross-section (see scanning electron microscope image of the silk fibre sample pictured in Fig. 2b) and homogenous material properties, validated by tensile testing. When surrounded by air, dragline silk in its pristine condition can be seen as an optical fibre, with a reported refractive index n of around 1.55 in the visible spectrum [7] and can guide light as shown in Fig. 2c by total internal reflection with a refractive index contrast Δn of 0.55.



(a) (b) (c)

Fig. 2. (a) Dragline silk directly extracted from a female spider by the Oxford Silk Group. (b) SEM image of the collected silk sample. (c) Native silk placed on a holder and used as an optical fibre.

First of all, we determined some optical specifications of dragline silk when used as an optical fibre. To obtain the transmission window of dragline silk, supercontinuum light (800 nm – 1700 nm) was coupled into a 2.5 cm sample by end-fire injection. Fig. 3a represents the total optical losses, obtained by subtracting the transmission spectrum, obtained at the output, from the spectrum measured at the input of the silk fibre. From this graph, one can easily notice that the transmission drops sharply beyond 1360 nm. The wavelength range with less propagation loss is 900 – 1100 nm. The relative loss (compared with the maximum transmission at 940 nm) in the C-band region is large (> 25 dB), making it more difficult to work at standard telecom wavelengths. The 1300 nm wavelength region appears to be a good compromise since the relative transmission loss is still low (< 10 dB) enough for performing measurement and optical components are more available in O-band than at 900 nm. We specifically measured the propagation losses of dragline silk at this wavelength, i.e. 1302 nm, by using a distributed scattering loss technique [8]. The intensity variation of the scattered light was obtained by taking the peak intensity at each point along the propagation direction. Fig. 3b represents the relative scattered power as a function of position along the silk strand. From this plot, the propagation loss is estimated to be 9±2 dB/cm in the O-band. Finally, wavelength scanning [9] was used to measure the birefringence of the silk fibre. Linearly polarised light from a tunable laser was launched inside the silk fibre and the transmitted light analysed with a polarization analyser. Detuning the wavelength of the input light induced a change in the phase difference φ between the two orthogonally polarized modes of the light transmitted. Fig. 3c shows the phase change φ against wavelength. From this graph, a high birefringence of 8×10^{-3} was determined at 1302 nm.



(a) (b) (c)

Fig. 3. Optical characterisation of the silk thread. (a) Transmission window of the silk fiber, (b) relative intensity of scattered light against longitudinal position and (c) phase change φ between the two orthogonally polarised light against wavelength.

Detecting chemical species with spider silk threads

Spider silk can be used as a very tough, biocompatible optical fibre for medical purposes and in biological media, since optical propagation was demonstrated in silk fibres, immersed in physiological liquid [4]. Moreover, these biological optical fibres can also be used for chemical sensing. In fact, in current fibre-optic sensing systems silica fibres are solely used as waveguides to bring light to and from the sensing region (chemically sensitive fibre-tip or coated fibre coating, activated by the evanescent-field leaking out of the silica fibre) and not as a sensitive element as such. Unlike the chemically-inert silica fibres, spider silk is a reactive protein thread and can interact with the surrounding environment in its pristine condition. Being composed of alternating blocks of α-helical (hydrophilic) and β-sheet (hydrophobic amino acids) domains [10], interacting molecules with these regions can either bind to the α-helical portion; thereby affecting the elongation properties of the fibre or the orientation of the crystalline β-sheet blocks. Therefore, a multitude of different chemical compounds can be detected using silk fibre. For instance, humidity can alter its mechanical properties – the latter even "supercontracts" in high humidity conditions (> 70% relative humidity levels at room temperature) [11].

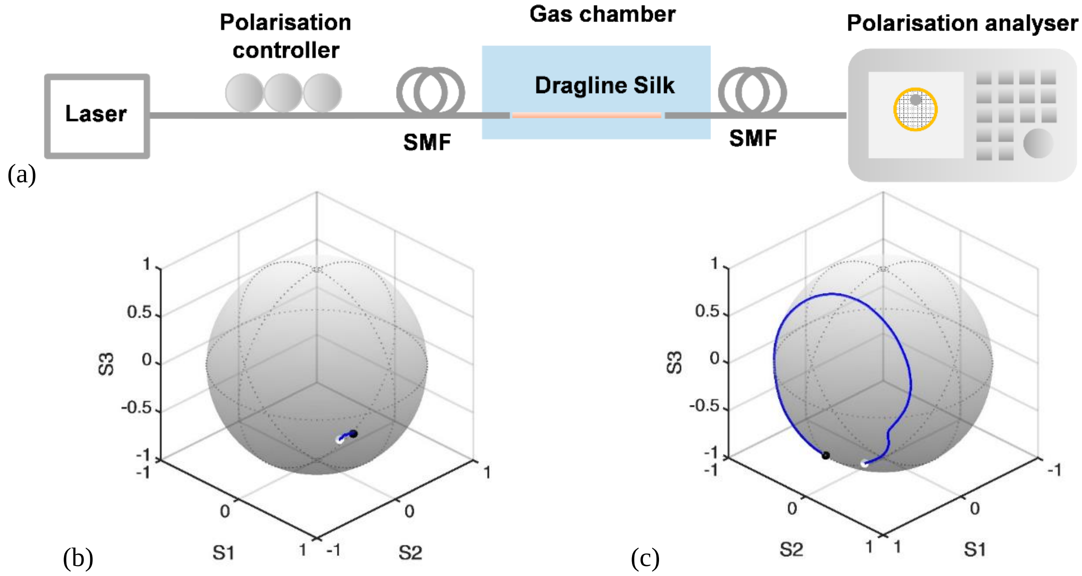


Fig. 4. (a) Experimental setup to measure the induced birefringence of the transmitted light along a dragline silk fibre brought by the presence of a biochemical agent. Evolution of the state of polarisation of the output signal on a Poincaré sphere when the silk thread was exposed to a (a) non-polar and (b) polar chemical vapour. *White dot: initial state of polarisation; Black dot: final state of polarisation; blue line: path along sphere.*

The experimental setup, represented in Fig 4a, was used to determine if silk threads could be used as chemically-sensitive optical fibres. A linearly polarised light was launched into the silk fibre and the state of polarisation (SOP) of the output light was analysed using a polarisation analyser. The silk thread was carried out in a hermetically tight gas chamber to isolate the silk thread from varying ambient conditions (pressure, humidity level, temperature), which could affect our results. The presence of non-polar molecules did not impact the silk fibre's birefringence. When exposed to pure carbon dioxide gas, the SOP of the output light barely changed; only a negligible drift, probably due to the effect of temperature on the lead fibres outside the gas chamber, was observed (Fig. 4b). On the other hand, as soon as hydrogen bond-active chemical agents, such as water and ammonia vapours, were introduced inside the gas chamber, the SOP immediately changed in a similar way as depicted on Fig. 4c, which represents the evolution of the SOP of the output light when the humidity (water) content was slightly changed inside the gas chamber. We hypothesize that the presence of polar molecules in the close vicinity of a silk fibre disrupts the hydrogen bonds within and between molecular chains, causing a change in the silk's birefringence.

Discussion

The potential of dragline silk as a new type of optical fibre for detecting chemical agents has been explored in this communication. Since the elemental building blocks of dragline silk are proteins, the presence of chemical agents around the silk can directly modify the properties of the fibre material in its entire volume; thereby changing the properties of light propagating inside it. The promising results demonstrated in this communication can potentially bring a major breakthrough in the optical fibre sensing field. First of all, the use of an intrinsically chemically-sensitive fibre allows for simpler and cheaper sensing systems (transmission setups) as compared to more complex fabrication processes that are nowadays needed for the fabrication and deposit of sensitized fibre tips and coatings on silica fibres. The fact that silk can be artificially spun at ambient condition [1] paves the way for functionalized silk, which can be made even more sensitive and selective by careful selection of protein composition or the incorporation of specific dyes, which would have been denatured at the very high drawing temperature required for silica fibres, in the bulk material.

Acknowledgement

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