

Weaving our way towards a new generation of fibre-optic chemical sensors based on spider silk

(Invited paper)

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Abstract—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 preys on its web. Indeed, this primeval material has been shaped over hundreds of millions of years by spiders to create a myriad of silk fibre types with different level of toughness, elasticity, stickiness depending on its attributed function in the web. From a human perspective, scientists are currently working on harnessing all the extraordinary properties of this material for applications spiders would never thought of, from biocompatible tissue engineering (enhancement of skin regeneration and nerve guides) to biodegradable electronics and development of specialised textile and composites. However, the potential of using spider silk fibre for chemical sensing has been overlooked. In this communication, we will explore the potential of using spider silk as a new type of fibre optic chemical sensor in a fully bio-inspired approach.

Keywords—spider silk; dragline silk; chemical sensing; polar molecules; induced birefringence.

I. INTRODUCTION

Fibre-optic chemical sensors (FOCs) are optical fibre-based devices used to measure chemical agents and biological molecular species such as proteins, nucleic acids, etc. and are promising alternatives to conventional bio/chemical sensors because they encompass all the advantages linked to the use of optical fibres including low cost, compactness, potentiality for remote and distributed sensing, etc.

The working principle of FOCs requires direct interaction between light and the target chemical substance. Generally, the optical fibre is solely used as convenient photon transport vectors [1]. For FOCs using sensitive fibre tips (Fig. 1(a)), they are only used to transport light from the optical source to and from the sensing region in order to detect the adsorption-induced change of the reflectivity brought by the presence of the bio/chemical compound. For instance, a MFI zeolite film can be grown on the end surface of an optical fibre [2] for TNT vapour detection. Another way to create light-gas interaction in the fibre’s surrounding is to force the light to

confine inside a thin optical fibre, with part of the light propagating outside the fibre (Fig. 1(b)). Hence, the sensitivity of these sensors depends on Φ , the fraction of the optical power present in the evanescent field as compared to the total optical power. Conventional optical fibres used for telecommunications being mainly intended for light propagation with minimal loss, the evanescent field is entirely contained within the cladding, thus not allowing light interaction with chemical species surrounding the fibre. Even if the cladding is removed, Φ remains too small for sensing applications, as a result of the high refractive index contrast.

Table 1: Different methods currently used to increase the interaction between the light evanescent field and the biochemical species.

Method	Basic principle
Sensitive material [3]	Passive cladding is replaced by a sensitive material
Sensitive cladding [4]	Cladding is specially designed to be sensitive to species to be detected
Fibre tapering [5]	Core/clad is reduced to increase the evanescent field magnitude and penetration depth.
Fibre bending [6]	Bending results in light loss and increase in evanescent field
Launch angle [7]	In multimode fibres, light can be launched at different angles (several modes).
Working wavelength [8]	Penetration depth increases with wavelength

Several techniques, summarized in Table 1, can be used to enhance the evanescent field and facilitate mode coupling for increased sensitivity. However, all these solutions rely on the evanescent part of the electromagnetic field for detection and are therefore limited in their effect since they use only a small fraction of the total field for interaction. For an extended evanescent field, tapered fibres with sub-micron diameters

must be used, but they are generally difficult to handle and have a short lifetime since their losses can increase up to 20-30 dB due to exposure to environmental factors such as humidity, dust particles, etc.

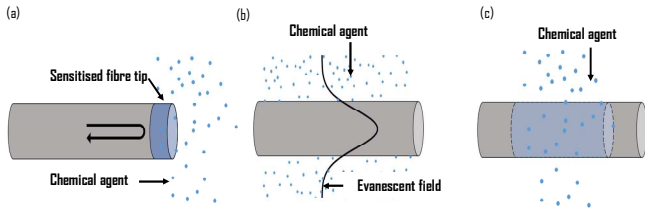


Fig. 1. Typical fibre-optic chemical sensors based on (a) sensitised fibre tip and (b) evanescent field sensing. (c) Proposed simplified interrogation technique based on a “chemically-sensitive” fibre. The presence of the target chemical agent modifies the material properties of the fibre, which can be quantified by analysing the properties of light transmitted along the fibre.

A more disruptive approach would be to directly use the optical fibre itself as the sensing element. The chemical agents would then directly modify the properties of the fibre material in its entire volume; thereby changing the properties of light propagating inside the fibre. The general principle of such a sensor is outlined on Fig. 1(c): light from an optical source is injected inside the sensing fibre, the agent will interact with the fibre material and any induced change in the fibres properties due to the presence of the agent will subtly alter the parameters of the transmitted light (intensity, wavelength, phase, spectrum, polarisation) in the fibre, which can be analysed and interpreted. Subsequently, the architecture of the sensing system is considerably simplified, since no evanescent-field coupling is required and the entire optical field interacts with the chemically sensitized material, therefore it is less energy-consuming compared to current optical fibre chemical sensors [9]. Moreover, a transmission setup excludes the risk of any contamination by other unwanted agents or dust since light is strictly kept confined inside the fibre.

II. PRISTINE SPIDER SILK OPTICAL FIBRES

A. Why use spider silk?

Hence, the underlying idea here is to choose an optical fibre made of a material, whose mechanical and optical properties would be potentially altered in the presence of biochemical agents, therefore paving the way for the use of a chemically reactive fibre, which is capable of interacting with its environment. Horse hair has long been known to expand with increasing humidity forming the basis of old hygrometers. Also, natural industrially available fibres like cotton, flax and wool are sensitive to humidity. However, these fibres contain a lot of impurities, like waxes, fatty acids, polyphenols, sugars, etc., and are generally cross-linked, thus making them less sensitive for sensing environmental compounds. In contrast, the industrially obtained silk from the silk moth *Bombyx mori* is a good candidate, but like the aforementioned fibres, it has an irregular cross-section (triangular), making them less suitable for light coupling.

Spider silk, however, represents the perfect candidate as it does not have any of the aforementioned shortcomings and possesses all these necessary characteristics for sensing chemical agents:

(i) Their ability to guide light has very recently been demonstrated in the region of 800 nm [10] and 1300 nm [11] by direct coupling, thereby paving the way towards the use of spider silk fibres for optical sensing.

(ii) Spider silk is composed of alternating blocks of α -helical (hydrophilic) and β -sheet (hydrophobic amino acids) domains [12]. 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 compounds can be detected with only a single silk fibre as many different interaction modes are possible.

(iii) The amount of crystalline and amorphous regions in the fibre can be consistently tuned in a very cost-effective way by changing the reeling speed and environmental conditions at ambient conditions. Thus, silk fibres can potentially be custom-made with a known amount of crystalline and amorphous regions to make it more/less sensitive to targeted chemical agents.

B. Dragline Silk as Optical Fibre

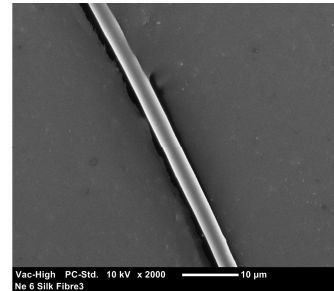


Fig. 3. Scanning electron microscope (SEM) image of a collected silk dragline

For our experiments, a single strand of silk of the major ampullate gland from a female *Nephila edulis*, reeled by the Oxford Silk Group under controlled conditions, was used. This species of spider was used for the following reasons: (1) *Nephila edulis* is one of the best studied species and best documented in the literature; (2) this spider species produces one of the thickest silk fibers, making them easier to handle; (3) this silk can be reeled under controlled conditions, such as reeling speed, humidity and temperature, in order to produce very uniformly spun fibres with a smooth surface, equal circular diameters and identical material properties, which is of vital importance for its optical properties as shown on Fig.3. Silk fibres with a diameter of 5.6 μm were collected for our experiments. When surrounded by air, the silk, with a reported refractive index n of around 1.55 in the visible spectrum [13], is intrinsically an optical fibre and guides light



Fig. 2. A female *Nephila edulis* spider

by total internal reflection with refractive index contrast Δn of 0.55.

III. OPTICAL CHARACTERISATION

A. Optical Transmission Window

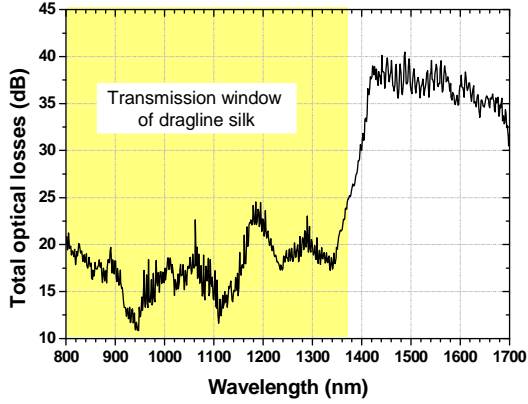


Fig. 4. Transmission window of the silk fiber.

Supercontinuum light (800 nm – 1700 nm) was injected into a 2.5 cm dragline silk sample and the resulting transmission spectrum, collected at the output of the silk sample, was measured. Fig. 4 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 transmission at 940 nm) in the C-band region is large (> 25 dB), making it more difficult to work in this transmission window. 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.

B. Propagation Loss

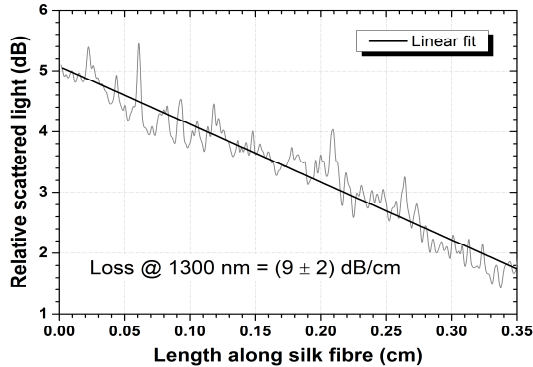


Fig. 5. Relative intensity of scattered light against longitudinal position.

The distributed scattering loss technique [14], which consists in measuring the intensity of scattered light from a fibre as a function of position, was used to measure the

propagation loss of silk fibre. The intensity variation of the scattered light is obtained by taking the peak intensity at each point along the propagation direction. Fig. 5 represents the relative scattered power as a function of position along the silk strand at 1302 nm. From this plot, the propagation loss is estimated to be 9 ± 2 dB/cm in the O-band.

C. Birefringence

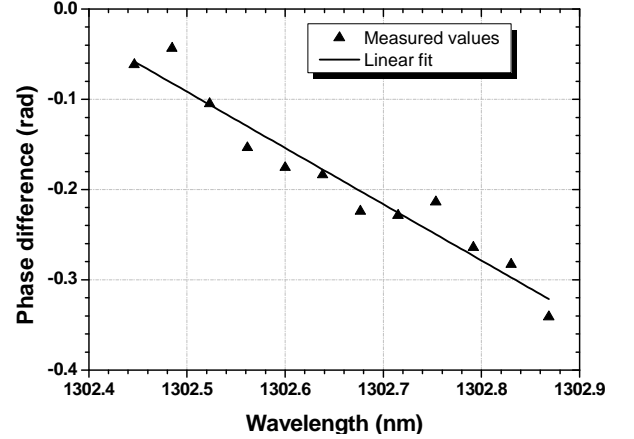


Fig. 6. Phase change ϕ of transmitted light against wavelength.

In order to measure the birefringence of the silk fibre, a method based on wavelength scanning [15] was used. Light from a tunable laser is launched inside the silk fibre and the transmitted light is analysed with a polarization analyser. Detuning the wavelength of the input light induces a change in the phase difference ϕ between the two orthogonally polarized modes of the light transmitted. Fig. 6 shows the phase change ϕ against wavelength. From this graph, a birefringence of 8×10^{-3} is calculated at 1302 nm.

IV. DETECTION OF CHEMICAL AGENTS WITH THE SILK FIBRE

The birefringence B of the silk fibre depends on both the overall degree of molecular orientation and the extent to which crystalline regions are present. Hydrogen bonds, within and between molecular protein chains, play a crucial role in the silk's structure. The presence of polar elements will gradually modify these bonds, causing the molecular chains to disorient and coil-uncoil [16]. This will change the overall molecular orientation inside the silk fibre and, therefore, induce a change ΔB in its birefringence. This change in birefringence will induce a change in the phase difference $\Delta\phi$ between the two orthogonally polarised modes according to the following equations:

$$\Delta\phi = \frac{2\pi}{\lambda} (\Delta L \cdot B + L \cdot \Delta B) \quad (1)$$

$$\Delta L = 0 \Rightarrow \Delta\phi = \frac{2\pi}{\lambda} \cdot L \cdot \Delta B \quad (2)$$

Note that a change in the length ΔL of the silk fibre (length L) can also induce a change in the phase difference $\Delta\phi$. In our case, we can neglect this change since the fibre is placed under strain and tightly fixed at both ends. By measuring this value of $\Delta\phi$, the change in birefringence can easily be deduced using equation (2). The change in the phase difference between the two orthogonally polarised modes of light propagating along the silk fibre can be obtained by monitoring the SOP of the transmitted light using a polarisation state analyser. The experimental setup, represented in Fig 7, was used to detect several chemical agents which impact the hydrogen bonding between the silk proteins within the silk fibre. A linearly polarised light at $\lambda = 1302$ nm was launched inside the silk fibre and the transmitted light was sent to a polarisation analyser. A cotton bud soaked with the targeted biochemical agent was then placed close to but not in contact with the silk fibre to allow vapour-silk interaction while simultaneously recording the SOP of the light guided through the silk fibre every 0.1 s for 15 s.

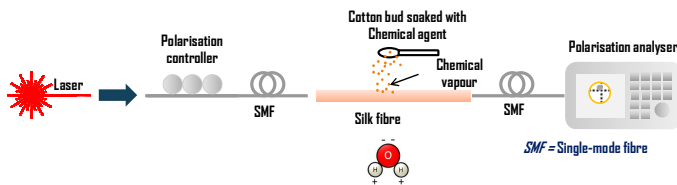


Fig. 7. Experimental setup to measure the induced birefringence of the transmitted light along a dragline silk fibre brought by the presence of a biochemical agent.

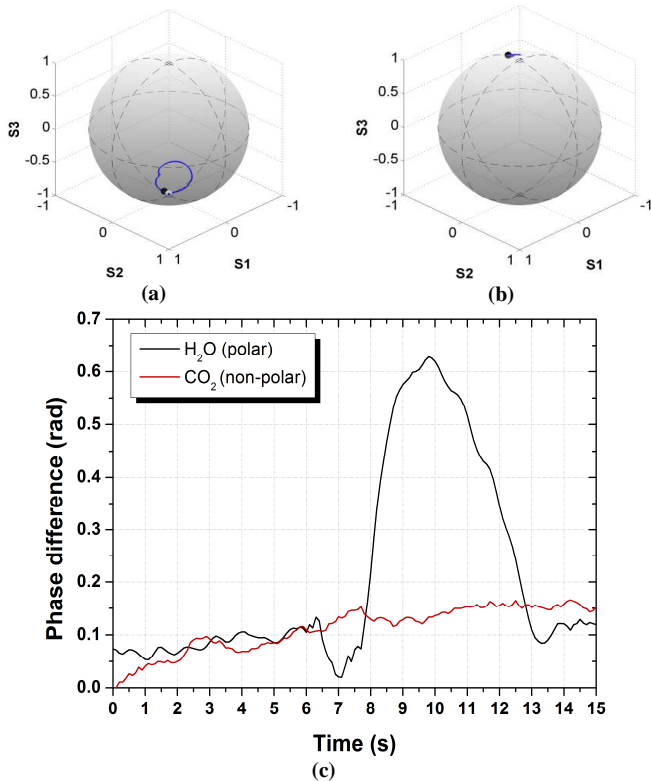


Fig. 8. Representation of the polarisation transformations on a Poincaré sphere of the transmitted light due to the presence of (a) water and (b) carbon dioxide vapours and (c) corresponding temporal changes in phase

difference $\Delta\phi$. White dot: initial state of polarisation; Black dot: final state of polarisation; blue line: path along sphere.

As soon as a cotton bud, soaked with water, was placed next to the silk fibre the SOP of the transmitted light instantaneously changed (Fig. 8(a)) indicating a change in the fibre's birefringence. The temporal evolution of ϕ for this experiment is plotted on Fig 8(c). Initially, the value of ϕ was constant since the silk fibre was left unperturbed. After 6 seconds, the cotton bud was placed next to the silk fibre. ϕ immediately changed with a response time of the order of the second and went back at to its initial phase when the cotton bud was removed.

On the other hand, the presence of non-polar molecules do not impact the birefringence silk fibre. When exposed to pure carbon dioxide gas, the silk fibre's birefringence did not change. Only a small drift, probably due to temperature, in the SOP of the transmitted light was observed (Fig. 8(b)).

Two other hydrogen bond-active agents, namely acetic acid and ammonia, were tested and the corresponding Poincaré representations showing the change in SOP in each case is shown in Fig. 9. Based on these figures, it is clear that the chemical agents induced a change in birefringence in the silk fibre. The corresponding change in birefringence ΔB , induced by these three chemical compound, was determined and listed in Table 2.

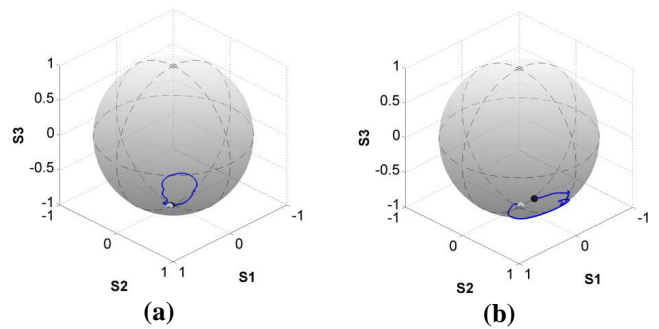


Fig. 9. Representation of the polarisation transformations on a Poincaré sphere of the transmitted light brought by the presence of (a) acetic acid and (b) ammonia vapours.

Table 2: Induced birefringence by each chemical compound.

Modifying agent	ΔB	Percentage change (%)
Water	5.11E-5	0.121
Acetic acid	4.59E-5	0.109
Ammonia	6.38E-5	0.151

V. CONCLUSION

The potential of dragline silk as a new type of optical fibre, able to detect chemical agents, has been explored in this communication. Dragline silk can indeed be used as an optical fibre and some of its optical properties were measured, for e.g., transmission window, propagation losses (order of some dB/cm) and birefringence ($10^{-2} - 10^{-3}$). Since the elemental building blocks of dragline silk are proteins, the presence of some chemical agents can directly modify the properties of the fibre material in its entire volume; thereby changing the

properties of light propagating inside it. Sensing of several chemical compounds has been demonstrated by recording the change in polarisation state of output light. The observation of fast response and high sensitivity of silk fibre towards polar chemical compounds (water, ammonia etc.) has shown promising application for chemical vapour sensing. Polar molecules can modify hydrogen bonds within and between molecular chains, causing the latter to coil and uncoil. This effect will be translated into a change in the silk's birefringence, which can be detected by monitoring the state of polarisation of the transmitted light using a polarisation analyser.

The promising results demonstrated in this communication can potentially bring a major breakthrough in the optical fibre sensing field. Firstly, the use of a sensing fibre made from a chemically sensitized material such as silk will considerably simplify the interrogation and detection sensing system as compared to more complex setups, based on evanescent-field sensing and sensitized fibre tips. Secondly, this will pave the way for the fabrication of a new generation of economical and custom-made FOCs since spider silk can be spun at ambient conditions. Moreover, silks can be functionalized to be even more sensitive to any type of chemical or particular environmental quantities by incorporating specific dyes making them very cost-effective for potential artificial industrial production of silk-based fibres with unique properties.

ACKNOWLEDGEMENT

This work was done within the framework of the Ariadna study n° 14-6401 (The Silky Way) supported by the European Space Agency. The Oxford Silk group thanks ERC (SP2-GA-2008-233409) and AFOSR (FA9550-12-1-0294) for funding.

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