Magnetoresponsive Optical Fiber with Fuse-Effect-Induced Fluorinated Graphene Oxide Core

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1. Introduction

Polymer optical fibers (POFs) have been widely used in different applications, such as home networks, automobiles, optoelectronic devices, and sensing. [1] Despite presenting higher attenuation and weight than silica single-mode optical fiber (SMFs), the inherent characteristics of POFs (easy connectorization and superior flexibility) allow to fabricate various flexible devices in high safety conditions. [1–4] Thus, to overcome high attenuation and scattering problems, the optical power injected into the optical fibers should be increased. [1,3] However, light injection at extremely high power into POFs causes not only burning or damage of the interfaces between POFs and SMFs, but also a continuous self-destruction process of the POFs. This phenomenon called fiber fuse is a well-known effect in glass fibers in the fiber-optic scientific community, and until recently, it has been a problem without solution or recycling applications. [5] In 2014, Mizuno et al. observed the fiber fuse effect in POFs for the first time and clarified its propagation properties. [6–8] In the following years, intense research efforts were driven to sensing applications of the damaged POFs, targeting the influence of some physical parameters, such as temperature and strain, on the intensity of the light propagating within the POF. [9–11]
In a fused polymer optical fiber (fPOF), it has been assumed that the burnt core material caused by the fuse effect is a carbonized polymer because the perfluorinated graded-index POF (GI-POF) is composed of doped and undoped polyperfluorobutenylvinyl ether layers (cladding and core, respectively). However, due to difficulties in extracting the fused material without damaging it, almost no efforts have been made to study the fused material properties, resulting in its limited applicability.

In this work, the first study on the magnetic, electric, and material properties of the fused core of the GI-POF is presented. Moreover, a simple extracting method based on a chloroform bath is reported, which allows to perform a material analysis only on the fused material. The preliminary results obtained by Raman spectroscopy and secondary electron scanning electron microscopy (SE-SEM) reveal that this fused fiber core material has similar structural characteristics to those of graphene foams (GFs). An extensive study to justify this assumption is performed by additionally performing superconducting quantum interference device (SQUID) magnetometry, energy dispersive X-ray spectroscopy (EDS), and X-ray photoelectron spectroscopy (XPS) tests, allowing to conclude that the material originated inside the fPOF is actually fluorinated graphene oxide (FGO). Taking advantage of both optical and electromagnetic properties of this in-fiber-FGO, a fiber-optic magnetic field sensor was developed.

2. Results and Discussion

The fPOF was prepared using the experimental setup depicted in Figure 1a, comprising a laser source, optical isolators, an erbium-doped fiber amplifier (EDFA). After the fuse propagation, the fused material was separated from the optical fiber through the dissolution of the nonfused material by a chloroform bath method[12] (see Experimental Section), as depicted in Figure 1b.

![Figure 1](https://www.advancedsciencenews.com/)

Figure 1. Polymer optical fiber fabrication and material characterization. a) Schematic diagram of the generation of fuse effect in GI-POFs. b) Schematic diagram of the fused material extraction protocol with a chloroform bath; c,d) Cross-sectional SE-SEM images of the fPOF. The core has collapsed onto itself in a spirally fashion. e) Transversal SE-SEM image of an isolated core without cladding, showing the foamy nature of the material. f) XPS spectrum showing the 1s peaks of fluorine oxygen and carbon and the 2s and 2p peaks of silicon. g) F 1s peak showing a balanced contribution of covalent and semi-ionic F─C bonds. h) C 1s peak with a strong sp² carbon contribution and a low signal of C─O bonds. i) Raman spectra of the nonfused fiber, fused core, and fused core with probing laser attenuated (blue, green, and red spectra, respectively). Reduction of the FGO into rFGO occurs when probing the fused core with the Raman laser at full power, evident by the appearance of the 2D band.
The secondary electron scanning electron (SE-SEM) images of the fused fiber reveal a radial shrinkage of the fused core (Figure 1c,d). The core seems to acquire a corkscrew profile, reminiscent from the light propagation mode during the fuse. Figure 1e shows a profile of a fused core in which the cladding and over cladding layers were removed with chloroform (see Experimental Section). In this image, the formation of foamy structure, resembling that of laser-induced graphene (LIG) on polyimide, can be observed.[13,14] It is expected that, similar to graphene oxide (GO),[17] this is compatible with the high degree of oxidation measured by XPS and EDS. Moreover, the excitation laser for this measurement required an attenuation with a neutral density filter with OD = 2, otherwise the laser power would reduce the GO-like foam into reduced GO (rGO), as evident by the appearance of the 2D band at ≈2700 cm−1 (Figure 1i) and well reported in the literature.[18] Note that the shift in wavenumber for the spectrum with the full laser power is due to the thermal stress caused during the process. The observations from the different characterization techniques are compatible with a form of FrGO.[16]

The results of the magnetometry tests, depicted in Figure 2a, show the temperature dependence of the magnetic mass susceptibility (χmass) of the nonfused (gray) and fused (red) POFs, measured (following a field-cooling protocol) over the temperature range of 5–400 K and under an externally applied magnetic field (Hext) of 250 Oe. Throughout the whole temperature region inspected, the susceptibility of the fused fiber is nearly 10 times larger than that of the nonfused fiber. Both susceptibilities decreased smoothly with increasing temperature in the 50–300 K range. At low temperatures (below 25 K), there was a sharp increase on the susceptibility of the fused fiber. Such behavior is typical of paramagnetic component, which might arise from individual noncorrelated atoms or small magnetic clusters. However, surprisingly, at higher temperatures (350–400 K), a significant decrease (>20%) was observed for the fused fiber, in contrast with the nonfused susceptibility behavior, which remains nearly constant in this temperature interval. Such significant decrease suggests the onset of a magnetic transition, such as a ferro/ferri magnetic toward a paramagnetic state.

The occurrence of a magnetically ordered state on the fused fiber, in the 5–350 K range, is further supported by the isothermal magnetization versus external magnetic field (M(H)) curves displayed in Figure 2b,c. The raw isothermal M(H) curves presented a negative, temperature-independent diamagnetic component, which has been subtracted for clearer visualization in Figure 2b,c (raw M(H) curves are presented in the Supporting Information). The M(H) curves measured on field increasing

![Figure 2. Magnetic characterization of the fused fiber material. a) Temperature dependence of the mass magnetic susceptibility of the fused (red) and nonfused fiber (gray) under an external applied field (Hext) of 250 Oe. b) Isothermal curves representing the magnetization (normalized to total mass sample and subtracted by the sample-independent linear, diamagnetic component measured at 300 K) as a function of external applied field in the [−5, 5] kOe range, for the fused (red) and nonfused (gray) fibers, measured at 6 K. In the inset, the same data at the [−0.5, 0.5] kOe range are highlighted for clearer visualization of the magnetization behavior in the near-zero external applied magnetic field region. c) Isothermal curves representing the magnetization (normalized to total mass sample) as a function of external applied field in the [−5, 5] kOe range, for the fused fiber measured at 6, 20, 40, 60, 100, 200, and 300 K. In the top-left inset the same data are plotted in the [−0.5, 0.5] kOe range for clearer visualization of the magnetization behavior in the near-zero external applied magnetic field region. In the bottom-right inset, the coercive field (Hc), estimated from these M(H) curves, is displayed as a function of temperature in the [6, 300] K temperature interval.](image-url)
and decreasing at 6 K, revealed hysteretic behavior for both non-fused and fused fibers, whereas the fused magnetization presented significantly larger hysteresis, due to its larger remnant magnetization. The observed coercive fields ($H_c$) at 6 K are identical for the fused and nonfused, being 197 and 177 Oe, respectively. Besides the hysteretic behavior, typical of a correlated magnetic state, the linear slope observed for higher $H_{ext}$ can be attributed to a paramagnetic component—in accordance with the susceptibility behavior at low temperatures. The significantly larger (>10 times) maximum magnetization ($M_{max}$) for the fused fiber clearly also illustrates the magnetic susceptibility enhancement after fiber fuse. In addition, the isothermal curves measured at several temperatures, in the 6–300 K range, show that the hysteretic behavior is retained up to 300 K, supporting the presence of a magnetic correlated state up to 300 K. Interestingly, the $H_c$ temperature dependence can be well fitted by a $T^{-1/2}$ (Figure 2c inset), in accordance with the Stoner–Wohlfarth model for a set of monodomain particles.[19]

To sum up, the magnetic properties exhibited by the fused fiber are consistent with a magnetic system composed of diamagnetic term (which can be associated with Landau and core diamagnetic contributions), paramagnetic term (associated with defect-induced paramagnetic centers and paramagnetic Pauli contribution from conduction electrons), and a ferro/ferrimagnetic term (associated with the long/short-range magnetic interactions between the paramagnetic centers), as reported by Tuček.[20]

$$\chi_{mass} = \chi_{mass, dia} + \chi_{mass, para} + \chi_{mass, ferro/antiferro}$$ (1)

Intriguingly, there are no classical magnetic elements ($d$ orbital elements) present in the fused fiber, to which these magnetic correlation enhancements can be attributed to. However, recently, Tuček et al. have found the room-temperature magnetic correlations in hydroxofluorographenes, composed of C, F, H, and O atoms and with no $d$ orbital elements.[20] They have identified the source of magnetism in these organic compounds to be based on the creation of diradical domains, through an appropriate $sp^2$ orbitals functionalization stabilized by the presence of neighboring $–OH$ groups. Furthermore, on the basis of density functional theory, calculations, Tuček et al. mapped the magnetic correlation strength as a function of F and OH contents, resulting in two ferromagnetic regions for specific F and OH group contents, and, more recently, experimentally observed a ferro-to-paramagnetic transition at high temperature (383 K) in these 2D organic materials.[20] In the light of these new findings, it is suggested that a similar mechanism should be at the origin of the fused fiber magnetic behavior. Similar to previous reports, the fused fiber also seems to present a ferro-to-paramagnetic transition at $≈$400 K, although along a broader temperature interval, which might be a direct consequence of disorder (chemical, structural, strain, etc.) in the magnetically correlated regions.

Having demystified the fused fiber’s material and magnetic properties and taking advantage of having an FGO material embedded in an optical fiber, an optical fiber magnetic field sensor was fabricated by creating a Fabry–Pérot interferometer (FPI) with a standard SMF-28, a sample of the fPOF, and an UV cure adhesive (Figure 3). The characterization of the optical fiber sensor to magnetic fields was conducted on a setup similar to the one depicted in Figure 4a. With increasing magnetic field intensity (field direction equal to 0°), the measured spectral dip shifted to shorter wavelength (Figure 4b). As can be seen in Figure 4c, this magnetic sensor presented different magnetic field sensitivities, namely, (4.66 ± 0.02) pm Oe⁻¹, (0.322 ± 0.005) pm Oe⁻¹, and (0.033 ± 0.002) pm Oe⁻¹, within three magnetic field intensity ranges of 0–400, 400–2000, and 2000–10 000 Oe, respectively. This behavior suggests that the optical fiber sensor has a saturation limit for magnetic field intensity values higher than 2000 Oe, similar to the magnetic field for which the magnetization saturates for the fPOF material, at 300 K (Figure 2c).

As comparison, an identical optical fiber sensor was developed using a non-fused GI-POF instead, attaining a maximum sensitivity of (0.027 ± 0.002) pm Oe⁻¹, which is almost 100 times lower than the value attained with the fPOF sensor. Despite this, the maximum sensitivity value of the fPOF sensor’s (4.66 pm Oe⁻¹) is within the range of previous reported works on magnetic field sensing with optical fiber sensors.[21–26] Moreover, this value is almost =2.7 times more sensitive than a recently reported device based on this fused POF with the same dimensions,[27] corroborating the use of the fPOF and the proposed sensing structure to develop electrically passive magnetic field sensors at the point of measurement.

3. Conclusion

In conclusion, the material and magnetic characterizations of a perfluorinated GI-POF damaged by a fuse effect were demonstrated for the first time. First, the fused core in terms of its chemical, atomic-bonding, and microstructural properties was thoroughly studied, which allowed to conclude that the fused core should be a form of FGO. From this assumption, a magnetic characterization was performed with SQUID magnetometry, revealing magnetic behavior similar to what was already reported for fluorographenes at wide ambient temperatures. On the basis of these characterizations, an optical fiber magnetic field sensor with unique properties was developed. In addition to the fused material electromagnetic characteristics, this device takes advantage of the intrinsic characteristics of optical fibers, such as lightweight, small dimensions, electrical passiveness, biocompatibility, remote monitoring, and resistance to harsh environments. Despite the fused material being susceptible to temperature, any cross-sensitivity issues could be mitigated by placing a temperature sensor.
(e.g., fiber Bragg grating) in a parallel configuration. Thus, this work unveiled the structural properties and magnetic potential of POFs damaged by the fuse effect, establishing the foundations for future developments of complex devices (sensors and actuators) with a wide range of applicability in biomedicine, aeronautics, and telecommunications.

4. Experimental Section

**POF Fuse Effect Generation**

POF employed in the experiment was a three-layered perfluorinated GI-POF with a core diameter of 50 μm, a clad-ding diameter of 70 μm, and an overcladding diameter of 500 μm. It had a numerical aperture of 0.185, a core refractive index of 1.35, and a propagation loss of ≈0.25 dB m⁻¹. The fuse effect was initiated in the same manner as that detailed in the study by Mizuno et al. The light at 1550 nm, amplified to 27 dBm using the EDFA, provided the energy for the fuse initiation.

**Fused Material Extraction**

The fused material was extracted from the POF by immersing several samples in a chloroform bath, at ambient temperature. After 10 min, the nonfused material was dissolved, and the fused material was extracted using a tweezer, as depicted in Figure 1b.

**Fused Material Characterization**

The XPS spectra were acquired using an ultrahigh vacuum system with a base pressure of 2 × 10⁻¹⁰ mbar. The system was equipped with a hemispherical electron energy analyzer (SPECS Phoibos 150), a delay-line detector, and a monochromatic Al Kα (1486.74 eV) X-ray source. High-resolution spectra were recorded at a normal emission take-off angle and with a pass-energy of 20 eV, which provided an overall instrumental peak broadening of 0.5 eV. To avoid signal from a substrate, a bundle of naked cores was attached to a ring holder with a 7 mm inner diameter and a height of 3 mm to the substrate. For the fitting, Gauss–Lorentz line shapes were used, and the Shirley background was eliminated.

The SE-SEM was performed in a TESCAN VEGA3 microscope with a working distance of 15 mm and a 10 KeV electron beam. The EDS spectra were acquired with a Bruker XFlash Detector 410-M. A carbon coating was used to reduce the charge effect in the insulating cladding. The Raman spectra evolution with increasing applied magnetic field intensity. c) Absolute wavelength shift of the reflected optical spectrum for an applied magnetic field intensity within the 0–10 000 Oe range (zoom-in in the 0–400 Oe range).

Figure 4. Optical fiber magnetic field sensor characterization. a) Schematic representation of the magnetic field characterization setup. b) Reflection spectra evolution with increasing applied magnetic field intensity. c) Absolute wavelength shift of the reflected optical spectrum for an applied magnetic field intensity within the 0–10 000 Oe range (zoom-in in the 0–400 Oe range).
analysis was performed in a backscattering configuration on a Horiba HR800 micro-Raman spectrometer using a 600 lines mm\(^{-1}\) grating and the 441.6 nm laser line from a HeCd laser (Kimmon IK Series) equipped with a 50× objective (spot size \(\approx 2 \mu m\), NA = 0.7, Olympus). A neutral density filter with OD = 2 was used to attenuate the laser output power (from 13.00 to 0.12 mW) in order to prevent the reduction of the sample and temperature-induced strain.

**Optical Fiber Sensor Fabrication:** The optical fiber magnetic sensor, based on a Fabry–Pérot interferometer, was developed by butt-coupling a silica SMF (SMF-28e+ from Corning) with a fPOF sample (20.0 ± 0.5 mm), by means of a 3D manual translation platform. A UV cure adhesive (NOA76, Norland) was used to couple both optical fibers, acting as the Fabry–Pérot cavity medium. The cure was conducted by using a focused UV light source (comprising a UV LED, model M365LP1, and a collimator, model SM2F32-A, both from Thorlabs).

**Magnetic Field Sensor Characterization:** The sensor characterization to magnetic fields was conducted using a Hallbach-type variable magnet (MM-1000-52, Magnetic Solutions) to apply different magnetic field intensities and directions, and an optical interrogator (SM-125-100, Micron Optics) to monitor the spectral response of the sensor.

**Supporting Information**
Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**
The authors declare no conflict of interest.

**Data Availability Statement**
The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords**
fluorinated graphene oxide, fuse effect, magnetic sensors, polymer optical fibers

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