Flexible and robust low-loss selenium-based multimaterial infrared fibers towards CO$_2$ laser ablation

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Highlights
Low-loss selenium-based CO$_2$ laser energy-delivering fibers are presented
Flexibility and robustness-customizable CO$_2$ laser delivering fibers are presented
The fibers are fabricated via a hybrid multimaterial fiber process
The fibers are available in CO$_2$ laser fabric cutting and biological tissues ablation
Flexible and robust low-loss selenium-based multimaterial infrared fibers towards CO₂ laser ablation

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SUMMARY
A small-scale delivery medium for CO₂ laser energy with stable performance, flexibility, and high-strength is crucial in extreme laser processing environments, especially for minimally invasive surgery in high-humidity, twisty and narrow channels. Here, flexible and robust multimaterial infrared fibers made of selenium-based chalcogenide glasses and thermoplastic polymer were developed with a low loss of 7.18 dB/m at 10.6 μm. The resulting fibers were capable of stably delivering single-mode CO₂ laser with 0.42 W average power. Moreover, to achieve precise control over the fibers in the practical clinical environment, customized co-polymers of polyphenylene sulfone resin and polyvinylidene fluoride were used as the fiber built-in jackets. Consequently, the fibers exhibited hydrophobicity, thermostability, high tensile strength, and low bending stiffness. The results demonstrated that the fibers can be used to deliver CO₂ laser energy for fabric cutting and bio-tissues ablation, making them attractive for CO₂ laser material processing and minimally invasive laser surgery.

INTRODUCTION
It is challenging to achieve effective and precise material processing in complex environments and with various materials. In particular, performing surgical procedures in high humidity environment and narrow operating spaces, such as orthopedics, is problematic for both surgeons and patients (Lee et al., 2016). High-efficiency and contact-less laser processing technology plays an increasingly important role in industrial machining, clinical surgery, and other fields (Dubey and Yadava, 2008). In particular, the compact and lightweight CO₂ laser system with a special infrared (IR) working window (9.3-10.6 μm) can effectively process materials such as fabric (Diaconu et al., 2008), plastic (Kant et al., 2015), steel (Rajaram et al., 2003) and biological tissues (Parker, 2007), and has become an attractive laser source for the new generation of laser processing technology. Currently, CO₂ laser energy is typically delivered to the target location of material by traditional articulated arms, in many application scenarios (Polanyi et al., 1970). Such a complex and bulky energy-delivering medium limits the application of the processing system in narrow and complex cavities. Therefore, a small-scale, flexible, high-strength, and low-loss laser delivery medium is critical for CO₂ laser processing technology. In this regard, IR fibers with more compact structures are receiving increasing attention (Tao et al., 2015).

The fabrication of IR fibers involves multiple disciplines such as fiber optics, materials science, manufacturing engineering, and so on (Tao et al., 2012b). The laser beam output quality, corresponding to the laser energy density and uniform action on the material, is an important indicator for evaluating CO₂ laser fiber used for laser material processing. Typical crystalline fibers based on silver halide polycrystalline materials are typically fabricated by the hot extrusion method, which results in fibers with large core-diameter up to hundreds of micrometers. This leads to poor output beam quality, limited length, and low mechanical strength (Merberg, 1993). Moreover, hollow fibers, such as hollow waveguides (Inberg et al., 1998), negative curvature fibers (Kosolapov et al., 2011), and hollow Bragg fibers (Temelkuran et al., 2002), are also limited by complex manufacturing processes, low reproducibility, and poor output beam quality. Based on the thermal drawing method, IR solid-core glass fibers such as fluoride, germanate, and chalcogenide glass fibers can be obtained with high output optical beam quality by tuning the fiber cross-section sizes to achieve single-mode laser output (Tao et al., 2012a).

In addition, low optical loss, excellent flexibility, and robustness are essential properties for CO₂ laser delivery fiber to stably deliver laser energy in a moving and curved cavity channel. Some hollow fibers such as...
hollow waveguides and hollow Bragg fibers have a large diameter (usually greater than 1 mm) and therefore a large bending stiffness. In addition, the bending loss of hollow fibers is theoretically high. Hence, hollow fibers are not fully applicable to the clinical surgical environment owing to their high bending sensitivity and stiffness, although they have been commercialized in the medical field (Remacle et al., 2012). Chalcogenide glasses (ChGs) are transparent in the 0.7-20 μm wavelength range and are the only glassy materials that can cover the CO2 laser transmission window (Tao et al., 2015). The new concept of multimaterial fibers has been found to be effective in improving the mechanical robustness of IR fibers (Tao et al., 2012b). Typically, the multimaterial IR solid-core fiber fabrication processes require the preparation of fiber preforms via traditional rod-in-tube (Yang et al., 2010) and extrusion (Tao et al., 2014a) methods, which are then assembled with polymer jackets to produce robust multimaterial IR fiber via thermal drawing method. Preforms fabricated by the rod-in-tube method usually exhibit a rough core-cladding interface, resulting in high optical losses of the fibers. The extrusion method yields a preform with a high-quality and smooth core-cladding interface, but it tends to introduce impurities during processing, which also results in high optical losses (Tao et al., 2014b). Moreover, the double-crucible method allows for a one-step fiber fabrication process. The resulting fibers exhibit a high-quality core-cladding interface and high purity, corresponding to low optical losses, but less robustness owing to no protection of polymer jackets (Snopatin et al., 2009). Recently, a hybrid multimaterial fiber fabrication process combining the double-crucible method and the thermal drawing method has been proposed (Shabahang et al., 2017). In this approach, a cane with a high-quality core-cladding interface is obtained via the double-crucible method under low-temperature and high gas pressure conditions, which is then assembled with a polymer jacket to obtain a low-loss, robust IR multimaterial fiber by the thermal drawing method. In addition, the core-cladding diameter ratio of ChGs cane or fiber can be precisely controlled by varying the diameters of crucible assemblies (the cylindrical and annular nozzle channels) and adjusting the gas pressures in inner and outer crucibles, respectively (Kobelke et al., 1999). The mechanical properties of optical fibers, especially flexibility and robustness, are mainly derived from the elastic modulus of polymer jackets, which can be precisely modulated by polymer compositing techniques to suit the demand for flexibility and robustness of optical fibers in special application environments (Kim et al., 2004).

The present work addresses the main challenges as outlined above. In this article, a hybrid fiber preparation process was adopted to fabricate low-loss, flexible, and robust multimaterial IR single-mode fibers using selenium-based chalcogenide glasses (Se-ChGs), which exhibited excellent thermochemical stability and high laser-damage-threshold. By introducing co-polymers of polyphenylene sulfone resin (PPSU) and polyvinylidene fluoride (PVDF) with different ratios, the tensile strength and bending stiffness of the fibers could be modulated precisely, making the fibers more controllable for the practical clinical minimally invasive environment. The resulting fibers exhibited low losses in the CO2 laser transmission window and realized efficient processing of fabric and biological tissue. The proposed flexible and robust low-loss multimaterial IR fibers are expected to benefit clinical minimally invasive laser surgery in the future.

RESULTS AND DISCUSSION

Se-ChGs, compared with tellurium-based ChGs, exhibit better thermochemical stability, which makes them exhibit higher laser-damage-threshold, and cover a wide IR transmission window of 2-16 μm range (Zhang et al., 2004). Although tellurium-based ChGs cover a wider IR transmission window, they are costly and chemically unstable during the material purification process (Wang et al., 2011). Therefore, two Se-ChGs with compositions of G1:As40Se60 and G2:As38Se62 were selected as core and cladding materials. The 2 mol% difference in Se content between these two glasses decreased the difference in refractive index between the core and cladding materials, i.e., 2.776 and 2.760 at 10.6 μm, respectively. The glass transition temperatures (Tg) of G1 and G2 are 184°C and 169°C, respectively. These glasses are low-cost As-Se system glasses and easy to manipulate in terms of refractive index and thermomechanical properties. Purification by dynamic distillation (Su et al., 2019) was adopted to remove elements with high IR absorption coefficients, such as C, H, and O (Churbanov et al., 2011).

High-quality ChGs canes with core and cladding materials of G1 and G2, respectively, were fabricated via double-crucible method (Figure 1A). The resulting Se-ChGs canes with core-cladding diameter ratio of 1:3 were obtained, as shown in Figure 1B. As Se-ChGs are opaque in the visible window and the core-cladding interface is not visible owing to small refraction index contrast, the core-cladding diameter ratio of the Se-ChGs cane cannot be directly judged by an optical photograph of the cane cross-section. To visually verify the control of core-cladding diameter ratio by the double-crucible method, the cladding material was
replaced with As$_{37}$S$_{63}$ glass, which is transparent in the visible window. The entire fabrication process of As$_{37}$S$_{63}$/As$_{40}$Se$_{60}$ canes was similar to that of the Se-ChGs cane and their cross-sectional photographs are shown in Figure 1C. The core-cladding diameter ratios of 1:2 and 1:4 for As$_{37}$S$_{63}$/As$_{40}$Se$_{60}$ canes corresponded to the internal to external gas pressure ratios of 2:1 and 1:1, respectively.

The PPSU jacket was fabricated by commercially available PPSU film with a $T_g$ of 220°C, which is thermally compatible with $G_1$ and $G_2$. It was assembled into a preform with ChGs cane by thin-film rolling process. As high-$T_g$ materials have a large elasticity modulus in the GPa range, PPSU jacket may endow the fiber with high tensile strength, but also large bending stiffness, resulting in the fiber becoming less flexible (Park et al., 2019). The thermal compatibility of the polymer jacket with the ChGs is critical for the co-thermal drawing ability of these two materials. However, polymers with a low elastic modulus that are thermally compatible with ChGs have not been identified. To substantially improve the flexibility of the fiber, custom co-polymers were prepared comprised of PPSU and low-$T_g$ PVDF (by quality). The ratios of PVDF in the
resulting co-polymers were 10, 20, 30, and 40 wt.%. Higher PVDF quantity will lead to material phasing and thereby affect its thermomechanical properties. Owing to the lower elastic modulus of PVDF, the co-polymers exhibited low elastic modulus, stable thermomechanical properties compared to the PPSU mono-material, and compatibility with the ChGs.

The preform assemblies fabricated via rod-in-tube method were placed in an indoor drawing tower for fiber drawing to obtain 600-μm-diameter multimaterial IR fibers. The core and cladding diameters of Se-ChGs fiber were 30 μm and 90 μm, respectively. Figure 1D shows the photograph of Se-ChGs fiber with a PPSU jacket. The resulting Se-ChGs fibers with 30 μm core-diameter are suitable for single-mode laser transmission at 10.6 μm wavelength, according to optical fiber single-mode laser propagation condition.

The cross-sections of multimaterial As37S63/As40Se60 fibers and Se-ChGs fiber were characterized, as shown in Figure 1E. The details of the manufacturing process are provided in the Methods section.

The resulting IR fibers were optically characterized by IR spectra in the wavelength range from 3 to 14 μm. As shown in Figure 2A, the as-prepared Se-ChGs fiber exhibited excellent optical performance in the transmission window of 3-13 μm, with only O-H and H2O absorption peaks. The transmission is an absolute value and includes coupling losses and Fresnel losses. The impurity bands were caused by raw materials, and they can be alleviated by multiple distillation processes. These impurity absorption peaks were not distributed in the CO2 laser wavelength range and did not affect the CO2 laser power delivery of the Se-ChGs fiber. The results indicate that the proposed fibers were capable of delivering CO2 laser. The optical loss of Se-ChGs fiber was measured at 10.6 μm via the cut-back method. The results are shown in Figure 2B. The optical loss of the proposed Se-ChGs fiber was 7.18 dB/m at 10.6 μm, which was comparable to the lowest value reported for Se-ChGs fibers (Shiryaev et al., 2015). This indicates that the proposed fiber fabrication process and polymer incorporation did not introduce additional optical losses. Moreover, 15-cm-long Se-ChGs fibers with core diameters of 30 and 60 μm, respectively, were used to control the fiber output mode, corresponding to the output mode changing from single-mode to few-mode. The maximum output average power of 15-cm-long single-mode Se-ChGs fiber was 0.42 W without cooling condition, corresponding to the average input power of 0.89 W.

The bending losses of the resulting 20-cm-long and single-mode Se-ChGs fibers were measured on cylindrical molds of different diameters using a 10.6 μm CO2 laser source. The bending angle was 90°, and the transmission was an absolute value including coupling losses and Fresnel losses, as shown in Figure 3A. All fibers can be bent to 1 cm, and the fiber maintained a stable laser transmission capability for a bend radius greater than 2.5 cm. As the bend radius decreased, the transmittance decreased significantly. The bend loss of the fiber was estimated to be 2.5 dB at a bend radius of 1 cm.

The mechanical properties (robustness and flexibility) of the fibers mainly stem from the polymer jacket of the fiber. The multimaterial IR fibers with different component ratios and 600 μm diameter were mechanically characterized using an electronic universal testing machine. The results are shown in Figure 3B. The PPSU jacketed Se-ChGs fiber with a large elasticity modulus displayed excellent robustness. Moreover, it
could withstand a tensile stress of at least 10 MPa without breaking or fracture of the internal glass material, which is 1000 times higher than that of As$_2$Se$_3$ bare fiber (Tao et al., 2014a). The tensile strength of the proposed fibers decreased as the PVDF content increased. Nevertheless, the tensile stress of the surviving fiber with 40 wt.% PVDF content was in the order of 5 MPa, which was still a significant improvement over the As$_2$Se$_3$ fiber. The bending stiffness of the fiber $K$ is related to the area moment of inertia $I$ as follows:

$$K = E \cdot I$$ (Equation 1)

where $E$ is the effective elastic modulus of the fiber. The effective area moment of inertia of 600-μm-diameter fiber can be expressed by the following equation:

$$I = \frac{\pi \cdot d^4}{64}$$ (Equation 2)

where $d$ is the diameter of the fiber. The effective elastic modulus $E$ value of the fiber, corresponding to the slope of the stress curve during elastic deformation, decreased with the increase in the PVDF ratio in the fiber. This indicates that the introduction of PVDF significantly improved the flexibility of the fibers. The effective elastic modulus of 40 wt.% PVDF fiber was as low as 133.3 MPa, corresponding to the bending stiffness of $8.48 \times 10^{-7}$ N m$^2$. The results showed that there was a state of dynamic compromise between the robustness and flexibility of the multimaterial fiber. Hence, the robustness and flexibility of the fibers can be customized to adapt to the application requirements.

The durability test was conducted by varying the humidity (90% at 50°C) and temperature (20-70°C), respectively, in a constant temperature and humidity chamber. The results indicated that the optical and mechanical properties of the fibers were affected negligibly. Therefore, the proposed fibers exhibited excellent hydrophobicity and thermostability.

The feasibility of the resulting fibers for processing fabric and biological tissue was demonstrated using a 10.6 μm CO$_2$ laser. As shown in Figure 4A, 15-cm-long single-mode Se-ChGs fiber was used to deliver CO$_2$ laser for effectively cutting a commercial cotton fabric with a thickness of 0.1 mm. The cotton fabric was fixed on a ceramic plate and moved by moving the liftable breadboard. Figure 4A shows a neat 4-cm-long cut by 0.42 W laser cutting of the fabric. Moreover, the feasibility of this fiber in biological tissue ablation was demonstrated, as shown in Figure 4B. Fresh chicken bone and muscle tissues were ablated by 0.8 W CO$_2$ laser via 60-μm-core-diameter Se-ChGs fiber for five minutes. The carbonization at the fabric and tissue edges was owing to the material burning caused by the long laser pulse width (500 μs) of the laser source. This effect can be relieved if the short pulse CO$_2$ laser with a pulse width less than 100 μs is used, because the most efficient tissue cooling takes place when the laser pulse duration time is much shorter than the tissue thermal relaxation time (Frentzen et al., 2003).

**Conclusions**

In summary, flexible and robust low-loss Se-based multimaterial IR fibers were prepared for small-scale, robust, flexible, and stable CO$_2$ laser energy delivery mediums in the extreme environment. The resulting
fibers were obtained via an advanced multimaterial hybrid fiber fabrication process and exhibited low loss of 7.18 dB/m at 10.6 μm, single-mode laser delivery property, excellent customizable mechanical properties, hydrophobicity, and thermostability. These fibers were particularly demonstrated to be effective in biological tissue CO2 laser ablation, making them attractive for future minimally invasive CO2 laser surgery in vivo.

Limitations of the study
Even though the multimaterial IR few-mode fibers in this work are highly effective for CO2 laser biological tissue ablation, the average laser power is still lower than that of crystalline fibers and hollow waveguides. This is owing to the relatively low laser-damage-threshold and the Fresnel reflection at the fiber end caused by the high refractive index of ChGs. This work aims mainly to demonstrate the advantages of these multimaterial infrared fibers for minimally invasive CO2 laser surgery, in terms of robustness, flexibility, high output beam quality, and low-cost. More efforts are needed to enhance the output power of the fiber, such as research on IR materials and anti-reflecting film coating technology.
STAR METHODS

Detailed methods are provided in the online version of this paper and include the following:

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AUTHOR CONTRIBUTIONS

Y.Z. investigated, designed, and conducted the experiments. Y.Z. and C.L. fabricated the fibers. Y.Z., C.L., Z.R., and Z.L. tested the fibers. Y.Z., C.L., Z.R., Y.X., C.H., S.L., and L.Y. wrote the article with contributions from all authors. All authors discussed the results. G.T. supervised the research.

DECLARATION OF INTERESTS

A CHN granted patent application (CN110683753A) on the method has been filed. The authors have no relevant financial interests in this article and no potential conflicts of interest to disclose.

INCLUSION AND DIVERSITY

We support inclusive, diverse, and equitable conduct of research.

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STAR METHODS

KEY RESOURCES TABLE

| REAGENT or RESOURCE           | SOURCE                                | IDENTIFIER               |
|------------------------------|---------------------------------------|--------------------------|
| Chemicals, peptides, and recombinant proteins | CNBM (chengdu) Optoelectronic Materials Co., Ltd | www.cnbmcoe.com          |
| Arsenic                      | CNBM (chengdu) Optoelectronic Materials Co., Ltd | www.cnbmcoe.com          |
| Selenium                     | CNBM (chengdu) Optoelectronic Materials Co., Ltd | www.cnbmcoe.com          |
| Aluminum                     | Aladdin                               | CAS:7429-90-5            |
| Anhydrous AlCl3              | Alfa Aesar                            | CAS:7446-70-0            |
| Polyphenylene sulfone resins | Solvay                                | Radel® R-5000            |
| Polyvinylidene fluoride      | Jiangxi Daishing POF Co., Ltd.        | http://www.dspof.com     |
| Other                        | 10.6 μm plused CO2 laser              | Access laser AL-30D      |

RESOURCE AVAILABILITY

Lead contact
Further information and requests for resources and reagents should be directed to and will be fulfilled by the lead contact, Guangming Tao (tao@hust.edu.cn).

Materials availability
This study did not generate new unique reagents.

Data and code availability
- The data reported in this paper will be shared by the lead contact upon request.
- This paper does not report original code.
- Additional information: Any additional information required to reanalyse the data reported in this paper is available from the lead contact upon request.

EXPERIMENTAL MODEL AND SUBJECT DETAILS
This study does not use experimental models typical in the life science.

METHOD DETAILS

Glass preparation
The commercial raw materials of Se (5N grade) and As (6N grade) were heated at 220°C and 350°C for 2 h under vacuum for the removal of surface oxide impurities, respectively. The purified substances, along with 100 ppm Al (5N grade, metals basis) and 500 ppm AlCl3 (4N grade, trace metals basis), were subsequently sealed in a quartz ampoule pre-cleaned with HF under vacuum according to the designed glass formulation and synthesized in a rocking furnace at 650°C for 24 h. Al and AlCl3 were adopted as deaerator and dehydrogenator, respectively. ChG was quenched and loaded into one zone (zone A) of customized quartz tube with two separate zones for dynamic distillation. Oxide impurities (e.g., Al2O3) were retained in zone A due to their low vapor pressure, and hydrogen-related impurities (e.g., HCl) were removed due to their high vapor pressure. Finally, ChGs vapor was condensed in another zone (zone B). After distillation, the pure glass in zone B was homogenized in rocking furnace at 650°C for 6 h to obtain high-purity glass. The resulting bulk glass samples were polished to thickness of 2 mm, and their transmission spectra in IR window were obtained using a Fourier transform infrared spectrometer (FTIR, Thermo Fisher Scientific, Nicolet iS50).
**Preform fabrication**
The obtained G₁ and G₂ were isolated from water and oxygen in inert atmosphere (dry Ar₂ gas), loaded respectively into the inner and outer quartz crucibles, and heated to the glass softening temperature. Then, the temperature was reduced by about 15°C after the glasses were completely melted and homogenized, and dry Ar₂ gas pressure was applied in the inner and outer crucibles, respectively, as shown in Figure 1A. Finally, uniform Se-ChGs canes were obtained with length of 10 cm, diameter of 3 mm, and core-cladding diameter ratio of 1:3. The co-polymer particles were hot pressed into sheets near the softening temperature point, and polymer jackets with 12 mm outer diameter and 3 mm hole diameter were obtained by mechanical processing.

**Fiber thermal drawing**
The ChGs canes were embedded into the co-polymer jackets. The whole assembly, including the PPSU and ChGs cane assembly thermal-consolidated under vacuum, was placed in an indoor drawing tower for fiber drawing, as shown in Figure 1A, with drawing temperature of 350°C, preform feeding speed of 0.5 mm/min, and drawing speed of 0.16 m/min. The diameter of the fiber could be precisely controlled by real-time monitoring of high-precision laser diameter meter.

**Fiber testing**
The end facets of the fibers were polished using Al₂O₃, cleaned and dried, and then analyzed. The fibers were analyzed in the transmission window of 3–14 μm using FTIR, and the emitting IR beam from the FTIR was focused and coupled into 600-μm-diameter Se-ChGs fiber with 15 cm length by a gold-plated concave reflector of focal length f = 50 mm. A liquid nitrogen-cooled mercury–cadmium–telluride (MCT) detector received the output electromagnetic waves signal to obtain the transmission spectrum of the fibers.

The optical losses of straight and bending fibers were measured using a CO₂ laser (Access laser, AL-30D). A single-mode laser beam with a spot of 2.4 mm and divergence angle of 5.5 mrad was coupled into the Se-ChGs fiber via an aspherical ZnSe lens (f = 12.7 mm), and a pyroelectric detector was placed at the fiber laser output end to detect the laser power. The IR images of output beam projected on the screen outside the fiber output end were obtained using Fluke T1400 IR camera.

The fibers (600-μm-diameter) were mechanically characterized using an electronic universal testing machine (SHIMADZU, AGS-X50KN). Loading rates were 5–10 mm/min.

**QUANTIFICATION AND STATISTICAL ANALYSIS**
This study does not include quantification and statistical analysis.