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GaSe-doped polymer microfibre for second-order nonlinear optical processes

Yuxin Ma¹, Biqiang Jiang^{1*}, Xiao Xuan, Zhen Hao, Xuetao Gan^{1*} and Jianlin Zhao

Abstract

As the most fundamental, efficient frequency-mixing technology, second-order nonlinear optical effects have been extensively applied in the fields of advanced laser technology, microscopic imaging, and optical communication. However, overcoming the limitations of the centrosymmetric nature of traditional optical fibres and exciting second-order nonlinearity remains challenging. In this study, we demonstrate a functionally doped polymer microfibre to implement second-order nonlinear processes in an optical fibre system. Few-layer gallium selenide (GaSe) nanosheets with high nonlinear susceptibility $\chi^{(2)}$ are doped in polyvinyl alcohol (PVA) to fabricate the hybrid polymer microfibre, which enables strong second harmonic generation (SHG) and sum-frequency generation (SFG) with sub-milliwatt pump power. When pumped by a continuous-wave (CW) laser, the observable SHG signal was excited in the 1500–1630 nm wavelength range, exhibiting a theoretically predicted power dependence. The SFG response was also validated in the GaSe-doped PVA microfibre with the excitation of two CW pumps, with the signal intensity corresponding to the theoretical evolution tendency when the power and wavelength of the pump light were adjusted. Hence, developing GaSe-doped polymer microfibres provides a novel approach toward the fabrication and application of nonlinear optical fibre devices.

Keywords: Polymer microfibre, GaSe nanosheets, second-order nonlinearity.

Introduction

Second-order nonlinear optical effects such as striking frequency conversion processes hold considerable potential for various fields in terms of optical frequency converters¹, advanced lasers^{2–4}, biological imaging^{5–8}, and microscopy technologies^{9–11}. Second-order nonlinearity is also eagerly anticipated for applications in optical fibres but is extremely weak in conventional silica fibres because of the centrosymmetric nature of the material. With the emergence of two-dimensional (2D) nonlinear

nanomaterials, numerous materials, particularly gallium selenide (GaSe) and molybdenum disulfide (MoS₂), offer excellent performance in achieving efficient second-order nonlinear effects in silicon-based photonic and optoelectronic devices^{12–17}. In particular, the monolayer GaSe possesses a considerable nonlinear susceptibility ($\chi^{(2)}$) of more than 1000 pm/V in the infrared telecom band¹⁸, and the layered GaSe itself exhibits an explicit thickness dependence of second harmonic generation (SHG) response^{19,20}. Hence, GaSe nanomaterials can exhibit excellent second-order nonlinear effects with high-power pulsed pumps as well as with continuous-wave (CW) light sources assisted by the light field enhancement of photonic crystal cavities or metasurfaces^{12,21–23}. Inspired by the form of space light acting on bulk or film materials directly, developing optical fibres assisted by layered nanomaterials

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is a promising approach to overcome the limitation of the centrosymmetric nature of fibre materials for realising second-order nonlinear optical responses²⁴. Owing to the high-transmission and low-dispersion waveguide modes in the fibre system, the second-order nonlinear process enables effective enhancement by adopting diverse material-integration schemes involving surface coating^{25–29}, new hybrid waveguide forming³⁰, and internal embedding^{31–33}. The light field around the fibre interacts strongly with the layered materials under wavelength-scale conditions, which is hardly disturbed by the presence of materials with an atomic layer thickness.

Polymer optical fibres are considered excellent nanophotonic manipulation waveguides owing to their unique advantages, such as easy availability, low cost, high transparency, and good flexibility. High-quality polymer microfibres are obtainable by versatile methods, including electrospinning³⁴, chemical synthesis^{35–37}, electron-beam lithography³⁸, direct laser writing^{39,40}, three-dimensional printing^{41,42}, and mechanical drawing^{43–45}, with the available length of polymer nanofibres tens of times longer than the silica counterparts and photonic nanowires. The advantages of polymer nanofibres, such as strong light-field confinement, small scale, high-proportion evanescent field, small allowable bending radius, and excellent molecular interaction environment, indicate their considerable potential for use in miniaturised optoelectronic devices. Moreover, based on the extensive compatibility of polymer materials, functional doping technology in the manufacturing process can customise the fluorescence^{46–49}, plasmon^{50–52}, specific selectivity^{53–55}, and soft electronic^{56,57} properties of polymer micro-/nanofibres, which support effective light–matter interactions.

Herein, we present a scheme that uses GaSe-doped polymer microfibres to realise stable and repeatable second-order nonlinear processes. The hybrid polymer microfibre was directly drawn from a polyvinyl alcohol (PVA) solution doped internally with few-layer GaSe nanosheets, with strong second-order nonlinear signals excited and transmitted longitudinally along the axis of the microfibre. We successfully observed the nonlinear signal spectra of SHG and sum-frequency generation (SFG) under CW light at a sub-milliwatt pump power. By increasing the pump power, the signal intensities of SHG and SFG exhibited an increasing trend in accordance with the theoretical value. Furthermore, the tunable laser (TL) enabled frequency upconversion in the infrared C and L telecom bands. Hence, the proposed GaSe-doped PVA microfibre can be considered a novel optical fibre for second-order nonlinear parameter conversion processes, transforming the fibre medium integrated with diverse

nonlinear materials and facilitating the expansion of applications in light source generation, inverter laser systems, and optoelectronic microdevices.

Operation principle

Fig. 1 shows a schematic of the GaSe-doped polymer microfibre used to realise second-order nonlinear processes. The employed ϵ -GaSe in the PVA microfibre always maintains the non-centrosymmetry with an arbitrary number of atomic layer structures due to the AB stacking sequence; this characteristic has been exploited in extensive second-order nonlinear frequency conversion processes^{18–20} via the high second-order nonlinear susceptibility $\chi^{(2)}$ and low absorption coefficient ranging from 650 nm to 1800 nm. To diminish the scattering effect of the thicker GaSe nanosheets, GaSe nanosheets with fewer atomic layers were selected for doping the PVA microfibres. Incident light was transmitted from a tapered fibre probe prepared from a conventional single-mode fibre (SMF) using the flame stretching method. With the light coupling of the lead-in tapered fibre, the fundamental waves (ω_1 and ω_2) are coupled into and propagate along the PVA microfibre, strongly interacting with the internally doped GaSe nanosheets. The excited second-order nonlinear frequency-converted waves ($2\omega_1$, $\omega_1+\omega_2$, and $2\omega_2$) are collected by the lead-out tapered fibre probe. Furthermore, the doped GaSe was encapsulated and protected by a PVA waveguide to isolate it from air oxidation, effectively enhancing the stability of the nonlinear fibre devices. The entire working region of the microfibre device was arranged on a low-index magnesium fluoride (MgF_2) substrate to reduce absorption and scattering losses from the substrate to the fundamental wave and frequency conversion signals.

Device fabrications and characterisations

PVA has been used to draw microfibres owing to its

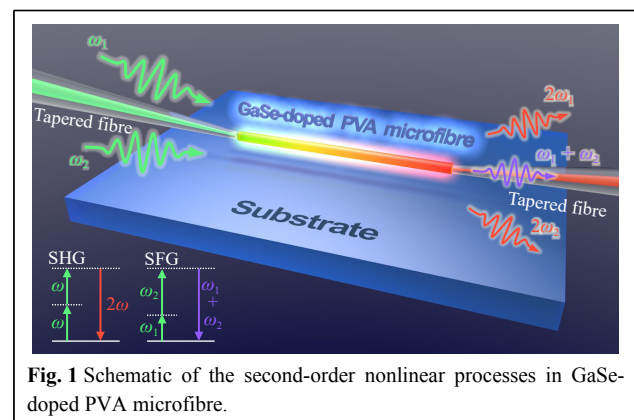


Fig. 1 Schematic of the second-order nonlinear processes in GaSe-doped PVA microfibre.

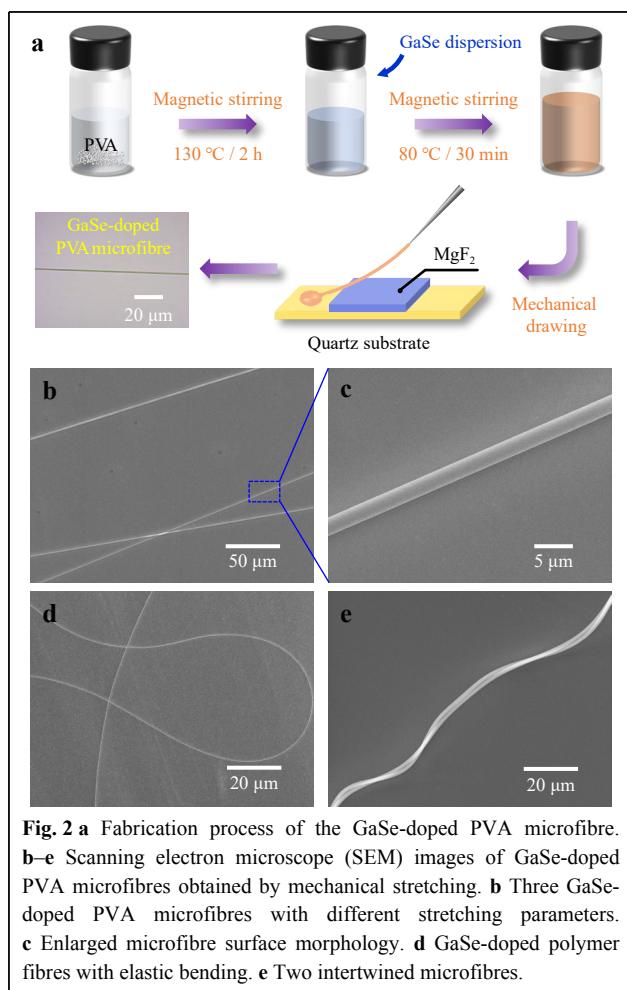
water solubility, good compatibility, and ease of fabrication⁵⁸. Fig. 2a shows the fabrication procedures of the GaSe-doped polymer microfibres, covering the steps of polymer feedstock preparation, GaSe doping, and microfibre formation. Centimetre-scale GaSe-doped polymer microfibres were obtained by mechanical stretching for further experiments. The morphology of the microfibres is an essential factor affecting their optical performance. Therefore, GaSe-doped PVA microfibres drawn with different process parameters were placed on a silicon substrate and characterised using scanning electron microscopy (SEM). As shown in Fig. 2b, the microfibres had homogeneous diameters over a long distance, with their excellent structural uniformity and low roughness observable in Fig. 2c (magnified region in Fig. 2b). Importantly, the parameters and performance of the GaSe-doped PVA microfibres can be reproducibly determined based on the needle tip size, solution-dipping volume, stretching distance, and moving speed. Moreover, flexible PVA microfibres could be shaped into specific states by

controlling the trajectory of the needle tip during the drawing process. Figs. 2d, e show several PVA microfibres maintaining elastic bending with a tight curvature radius with no structural fracture. Compared with other nonlinear nanowires, GaSe-doped PVA microfibres exhibit unique advantages in terms of customisable forming length, great flexibility, and high mechanical strength—all anticipated to extend their application fields.

To estimate the distribution of the doped materials, the microfibres before and after doping with GaSe were examined using transmission electron microscopy (TEM), with the results shown in Fig. 3a, b. As shown in Fig. 3a, the PVA microfibre without GaSe doping is pure and has smooth sidewalls—considered an excellent waveguide environment for second-order nonlinear processes. In contrast, the GaSe nanosheets (highlighted spots in Fig. 3b) were uniformly distributed in the doped PVA microfibre and did not affect the surface morphology of the polymer waveguide because of the much smaller size of the nanosheets. We also characterised the GaSe nanosheets to be doped using atomic force microscopy (AFM) and SEM before fabricating the GaSe-doped PVA hybrid microfibres. From the AFM and SEM images shown in Fig. 3c, the thickness and average size of the doped GaSe nanosheets were approximately 4 nm and <300 nm, respectively. Therefore, the possible modes of the light fields were effectively limited and transmitted in the polymer microfibres. In Fig. 3d, further elemental analysis by TEM shows that in addition to the PVA's own carbon and oxygen elements, the microfibres also contain significant amounts of Se and Ga. The difference in the contents of Se and Ga stems from the reduced electron energy and shortened exposure time of TEM testing to exempt the polymer microfibre from damage as well as the disturbance of unknown elements in the copper mesh substrate. Therefore, we can roughly determine the distribution of GaSe in the PVA microfibres using the TEM images.

Results and Discussion

A pair of high-precision displacement platforms were arranged to control the SMF probes for coupling with both ends of the GaSe-doped polymer microfibre. In the experiment, light coupling between tapered fibres and PVA microfibres was achieved using the direct connection method⁵⁹. Tapered fibre probes with diameters matching those of the PVA microfibres were drawn from a traditional SMF using the hydroxide flame heating technique. Through real-time observation using a charge-coupled device (CCD), tapered fibre probes were clamped by a pair of six-dimensional translation stages and then



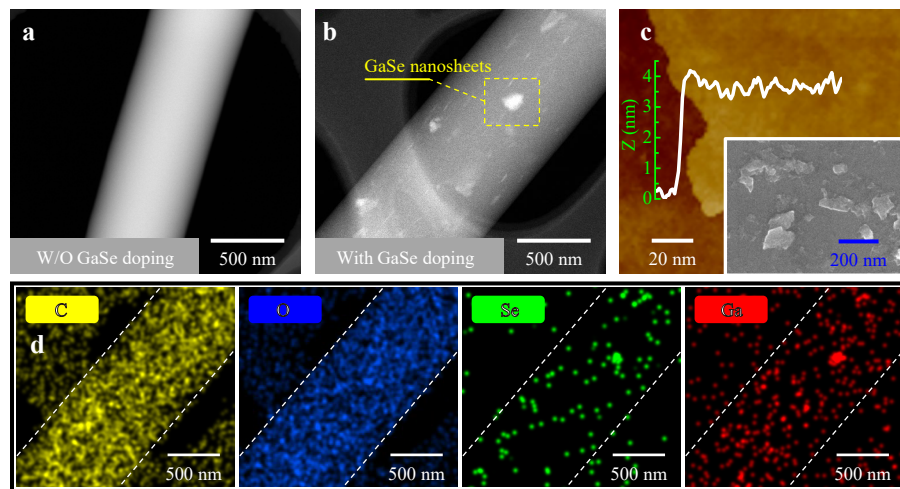


Fig. 3 Transmission electron microscope (TEM) images of **a** a PVA nanofibre without GaSe and **b** a 910 nm GaSe-doped PVA nanofibre; highlighted spots represent GaSe nanosheets. **c** Atomic force microscope (AFM) image of a GaSe nanosheet. The inset is an SEM image of GaSe nanosheets. **d** Distributions of C, O, Se, and Ga elements marked with different colours in the GaSe-doped PVA microfibre measured by TEM. Scale bars: 500 nm.

gradually approached the PVA microfibre. Simultaneously, transmission from the lead-out fibre probe was monitored using a power meter, with the maximum coupling efficiency determined by adjusting the tapered fibres fixed on the translation stages. The final coupling state is shown in Fig. 4a, where the fundamental wave source was incident on the polymer microfibre by the left probe, while the other probe on the right was used to collect the nonlinear signals derived from the interaction between the polymer microfibre and the doped GaSe nanosheets. The diameter of the employed microfibre is approximately 3.53 μm , as indicated in the inset of Fig. 4a (optical microscope image). Fig. 4b shows several microscopic views of the visible light transmission along the GaSe-doped polymer microfibre. The incident light of the 635 nm and 532 nm lasers caused a strong scattering effect on the side of the polymer waveguide (mainly derived from the excitation between the pump light and GaSe nanosheets). The pump light intensity decreases with increasing length of the GaSe-doped polymer microfibre, and the decay of the excitation light in the hybrid microfibre mainly originates from scattering and absorption caused by the GaSe nanosheets and polymer impurities.

To evaluate the light propagation performance of the GaSe-doped polymer microfibres, we measured the output power of microfibres of different lengths using a 1550-nm CW laser with a fixed pump power of 10 mW. Microfibres of different lengths were acquired from the same microfibre using the cutback method. As shown in Fig. 4c, the output power of the lead-out tapered fibre shows a

decline with increasing fibre length (following the Bouguer–Lambert law), and the loss coefficient of the output power is approximately $0.013 \mu\text{m}^{-1}$ (0.056 dB/ μm) by exponential fitting analysis, lower than other reported functionally doped polymer microfibres under 1550-nm pump light⁶⁰. During fabrication, the doping concentration of the nanomaterial must be considered for its impact on the nonlinear signal intensity. For nonlinear signal accumulation in the GaSe-doped PVA microfibres, a low concentration of GaSe doping may generate weak, even undetectable, nonlinear signals, whereas a high concentration would induce appreciable scattering from the agglomeration and overlapping of the doped GaSe nanosheets, thus highlighting a trade-off between the doping concentration of the GaSe nanosheets and the transmission loss. In addition, doping GaSe nanosheets with a smaller size and homogeneous dispersion is an effective approach to reducing the transmission loss of microfibres. Benefitting from the high transparency of PVA at the visible wavelengths, the transmission loss of SHG signals is expected to be less than 50%.

Considering the structure and waveguide dispersion of the PVA microfibre determine the properties of the supported propagation modes, we established a structural model of the PVA microfibre to further investigate the transmission properties in the polymer waveguide. According to the full-vector finite element method (FEM) analysis with the 1550 nm pump, we simulated the multiple possible modes allowed to propagate in the dopant-free PVA polymer microfibre, including the fundamental mode and five high-order modes, as shown in Fig. 4d. More

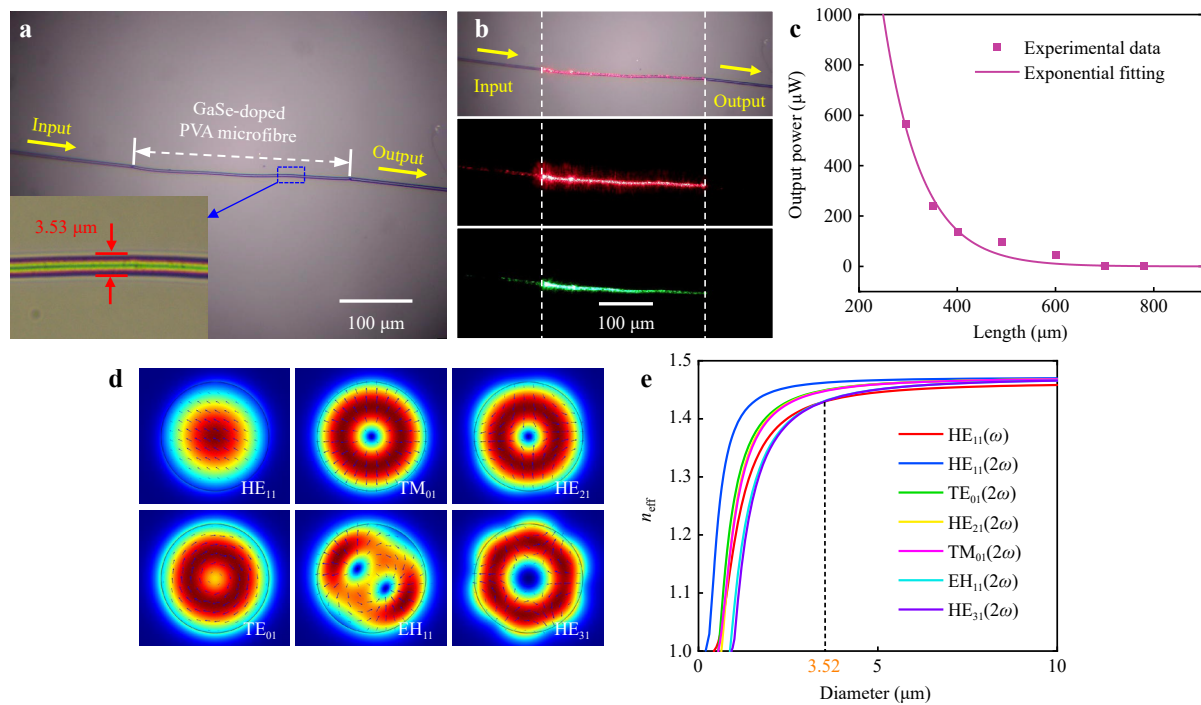


Fig. 4 Optical characterisation of GaSe-doped PVA microfiber. **a** Coupling image of 295 μm GaSe-doped PVA nanofibre observed by a CCD. Left-bottom inset shows the partial enlargement of the 3.53 μm polymer fibre. **b** Light coupling and propagation along GaSe-doped polymer fibre, launched by 635 nm and 532 nm lasers under bright/dark field. **c** Dependence of the output power from the doped microfiber on the propagation distance at 1550 nm. **d** Possible calculated transmission modes in PVA microfiber, including the fundamental mode and five higher-order modes. **e** Effective refractive indices of propagation modes with the fundamental wave (ω) at 1550 nm and possible second harmonic waves (2ω) at 775 nm in the PVA microfiber.

importantly, the conversion efficiency of SHG strongly depends on the phase-matching relationship between the fundamental wave (ω) and second-harmonic wave (2ω) related to waveguide dispersion^{26,61}. Next, we numerically calculated the effective refractive indices (n_{eff}) of the fundamental mode at 1550 nm (ω) and a few supported modes at 775 nm (2ω) under different microfiber diameters, with the results shown in Fig. 4e. The phase-matching condition involving the modes $\text{HE}_{11}(\omega)$ corresponds to $\text{EH}_{11}(2\omega)$ and $\text{HE}_{31}(2\omega)$, which belong to the same linear polarisation mode LP_{21} with the n_{eff} difference on the magnitude of 10^{-4} . Comparing the electric field distributions of the two mode pairs, while both enable supporting the frequency conversion in GaSe-doped PVA microfiber, the modes of $\text{HE}_{11}(\omega)$ and $\text{EH}_{11}(2\omega)$ may dominate the SHG process due to the higher overlap coefficient. As a result, the optimal diameter of PVA microfiber should be approximately 3.52 μm , consistent with the results shown in Fig. 4a. In addition, an optimal light-matter interaction length exists owing to the transmission loss of PVA with GaSe doping. As the microfiber length increased, the intensity of the nonlinear response first increased with cumulative signals and then

decreased because of the excessive transmission loss. Based on analysing and comparing the transmittivity of pump light and intensity of SHG accordingly, the 295- μm -long microfiber was selected for further experiments.

A measurement system was constructed to excite and detect the second-order nonlinear signals, including SHG and SFG, as shown in Fig. 5a. The pumped light from the laser was transmitted to the tip of the tapered fibre probe through a section of a common SMF and then coupled into the polymer microfiber placed on the MgF_2 substrate. The excited second-order nonlinear signals were collected using another lead-out tapered fibre probe. The coupling state was monitored in real-time using a CCD and displayed on the screen, as schematically shown in the top inset of Fig. 5a. A free-space filtering system, which consisted of two collimators of different wavelengths (1550 and 780 nm), a dichroic mirror, and a reflector, was arranged on the lead-out tapered fibre to extract the SHG or SFG signals from the mixed fundamental-frequency light. Consequently, only the SHG and SFG signals can be collected and analysed using a spectrometer that subtracts background interference in advance.

To verify the second-order nonlinearity of the GaSe-

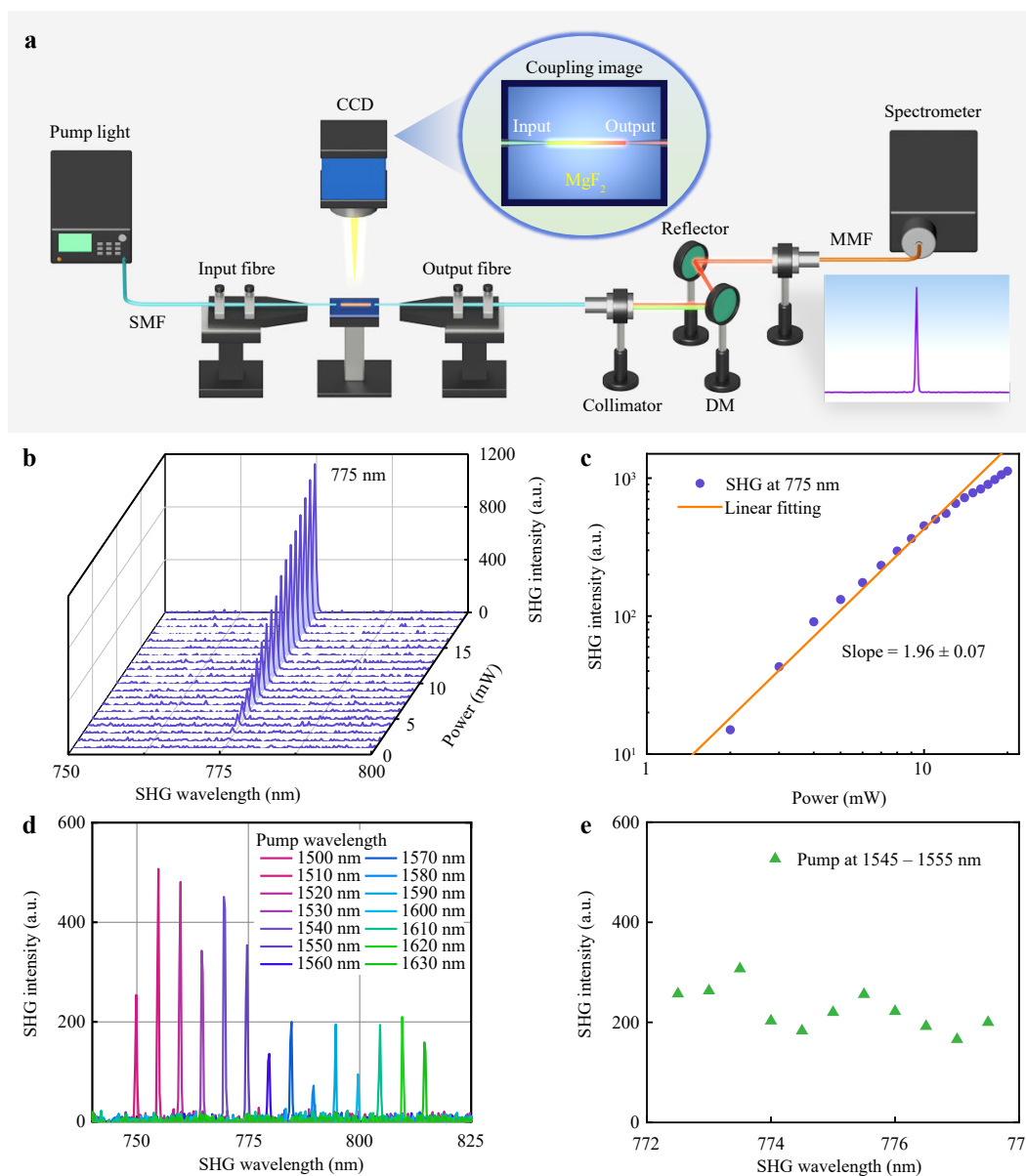


Fig. 5 Experimental setup and results of SHG in the GaSe-doped PVA microfiber. **a** Schematic of testing system for the second-order nonlinear signals. Coupling image in CCD is shown in the inset (DM: dichroic mirror). **b** Power-dependence of the SHG at 775 nm with 0–20 mW output power of the TL. **c** Corresponding log-log plot of the SHG intensity vs. incident power; the fitting slope is 1.96 ± 0.07 . **d** Spectra of SHG responses with pump tuned in the 1500–1630 nm range at 10 nm intervals. **e** Fluctuations of SHG intensity with 1545–1555 nm pump light. Pump tuning interval is 1 nm.

doped polymer microfiber, a CW-TL with a wavelength of 1550 nm was used as the light source to excite the SHG response. As expected, a significant SHG signal appeared at 775 nm. In general, conventional bulk nonlinear crystals allow the excitation and enhancement of second-order nonlinear signals, ensuring a long interaction length to satisfy the phase-matching condition; however, the nonlinear signals of on-chip devices assisted by 2D materials are severely limited by the short interaction

length with the pump light^{62,63}. The GaSe nanosheets were compatibly assembled in the PVA microfibres to increase the accumulated light–matter interaction distance for enhanced nonlinear responses. In schemes of pristine 2D materials and semiconductor nanowires, SHG usually requires a pump of high-power pulsed lasers, whereas, in GaSe-doped PVA microfibres, SHG can be observed with a low-peak CW pump^{3,64–67}. Further tuning of the TL output power revealed that the SHG signals exhibited power-

dependent characteristics, with the spectral variation shown in Fig. 5b. As the output power of the TL increased from 0 to 20 mW in intervals of 1 mW, the intensity of the SHG signal gradually increased. The log–log plot in Fig. 5c indicates the trend of the SHG intensity following pump light power changes, consistent with the quadratic dependence. The fitting slope of 1.96 ± 0.07 approaches the theoretical value of 2, and the imperfect quadratic dependence could be attributed to the slight change in the coupling state with the output power of TL exceeding 10 mW. When the TL was operating at 10 mW, the actual pump power in the microfiber was measured to be 0.567 mW, as shown in Fig. 4c. Then, the normalised SHG conversion efficiency is calibrated as approximately $\eta = 3.4 \times 10^{-4} \text{ pW}/(0.567 \text{ mW})^2 = 1.06 \times 10^{-7} \%/W$ using the reported calculation method^{68,69}.

In addition, we explored the wavelength dependence of the SHG signal by controlling the TL wavelength. Fig. 5d shows the SHG response with varying pump wavelengths, covering the entire C and L telecom bands. The high refractive index contrast between the PVA material and the external medium allows multimode transmission within the highly localised waveguide and relaxes the phase-matching conditions of the SHG processes²⁶. As a result, the GaSe-doped polymer microfiber is capable of exciting effective SHG responses in the wide pump wavelength range of 1500–1630 nm, and the fluctuations in SHG intensity in the broadband wavelength range can be attributed to crosstalk in multimode propagation and global modulation by the phase-matching condition²⁶. We also monitored the stability and reliability of the tunable SHG signal in the narrowband wavelength range of 1545–1555 nm, as shown in Fig. 5e. The stability of the SHG signals can be slightly disturbed by airflow vibrations from the environment.

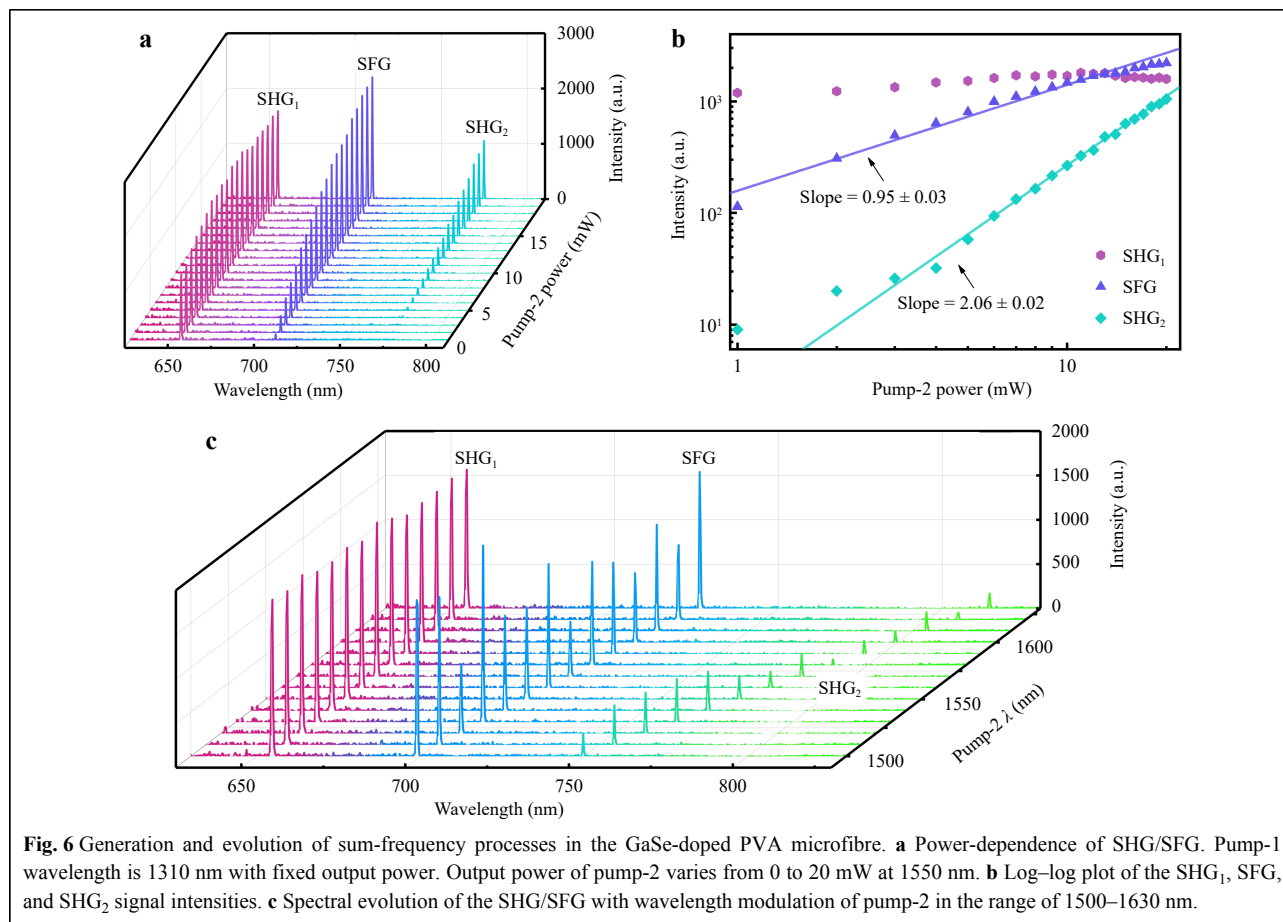
The implementation of the SFG parameter conversion process largely depends on the synchronisation of the two pump sources. The successful excitation of SHG with the CW source laid the foundation for exploring the SFG process, which was exempt from the synchronisation of pumps. Based on the testing setup shown in Fig. 5a, two CW pumps from different TLs, combined with a wavelength division multiplexer (WDM), were launched into the GaSe-doped polymer microfiber to replace a single light source. By fixing the output power of pump-1 with 1310 nm wavelength at 15 mW, we adjusted the output power of pump-2 with 1550 nm wavelength from 0 to 20 mW. Fig. 6a displays the spectral evolution of the second-order nonlinear processes with the power of pump-2 increasing in steps of 1 mW. The SHG signals at 655 nm (SHG₁) and 775 nm (SHG₂) are clearly observed in Fig. 6a, with the higher intensity of SHG₁ attributed to the low

transmission and coupling loss at shorter wavelengths. In addition to the SHG₁ and SHG₂ mentioned above, high-intensity SFG around 710 nm was excited at the same time, conforming to the theoretical wavelength.

The log–log plot in Fig. 6b clearly demonstrates the relationship between the different nonlinear signal intensities and pump-2 output power. Considering the pump-1 power remained constant, the SHG₁ signals did not change significantly but experienced a slight decrease owing to more photons participating in the SFG excitation during the increase of pump-2 power. Meanwhile, the intensities of SHG₂ and SFG tended to increase with increasing pump-2 power. The fitting slope of SHG₂ is 2.06 ± 0.02 , consistent with the results shown in Fig. 5c. Considering the SFG signal intensity only relies on the increments of tuning the 1550 nm pump, the fitting slope of 0.95 ± 0.03 is consistent with the conversion principle of the SFG process. In addition, the wavelength dependence was reflected in the excitation process of the SFG. With the output power of the two pump sources fixed, pump-1 was set to 1310 nm, operating at 15 mW, and pump-2, with a power of 10 mW, was adjusted to output wavelengths in the 1500–1630 nm range. Fig. 6c illustrates the spectral evolution with wavelength dependence of the SFG response. Apart from SHG₁ being extremely stable, the signal spectra of both SHG₂ and SFG appeared red-shifted as the pump-2 wavelength increased.

Conclusion

In summary, GaSe-doped polymer microfibres drawn directly from a mixed PVA solution effectively achieved internal second-order nonlinear optical effects. Owing to the low-damage mixing technique, the doped GaSe nanosheets significantly improved the light–matter interaction in the PVA microfiber, consequently allowing both SHG and SFG parametric conversion processes. By tuning the CW pump, we verified the pump power and wavelength dependence of the SHG signals in the 1500–1630 nm wavelength range, relying on relaxed phase-matching conditions and a high-refractive-index environment. The stable SFG was excited with two CW lasers, and its signal spectrum underwent the expected changing trend with laser power and wavelength modulation. The proposed hybrid polymer microfiber supports fibre integration with diverse nonlinear nanomaterials, such as InSe, MoS₂, and WS₂, and serves as a protective medium to ensure the long-term operation of susceptible materials. GaSe-doped PVA microfibres are expected to be manufactured with protective cladding coatings, reduced transmission, and enhanced coupling efficiency, thus providing more opportunities for their



practical use in applications involving signal processing, novel light sources, nonlinear optical imaging, and fibre sensing in complex environments.

Materials and Methods

The nonlinear polymer microfibres used in this study were fabricated by mechanical stretching using a GaSe-doped PVA mixed solution. The pure PVA aqueous solution was initially obtained by dissolving 1 g PVA powder into 4 mL deionised water at 130 °C under high-speed magnetic stirring for 2 h. GaSe nanosheets were dispersed in a solution of alcohol and deionised water at a concentration of approximately 1 mg/mL. To avoid the oxidation of GaSe nanosheets at a high temperature, which would affect the second-order nonlinear properties, the solvated PVA solution was cooled to 60–80 °C before adding the nonlinear materials. Next, 2 mL of the GaSe nanosheets dispersion (ultrasonicated for 15 min) was uniformly mixed in a PVA aqueous solution under magnetic stirring for 30 min at 80 °C to prepare the GaSe-doped PVA aqueous solution; this solution was sealed and allowed to stand for 24 h to eliminate air bubbles in the

solution caused by the high-speed stirring. After resting, a GaSe-doped polymer droplet was removed and placed on a slide at room temperature around 25 °C for approximately 1 h to allow the surface to solidify slightly; the needle-tip-like probe was immersed in it and then drawn directly to form the microfibres. The fabrication process was performed manually, with the microfiber performance determined based on the solution concentration, needle tip size, solution-dipping volume, stretching speed, and length. The employed microfibres with the desired diameter could be controlled within an error of 500 nm, with their doping concentration being almost consistent owing to the small size and low doping concentration of the GaSe nanosheets. Finally, a GaSe-doped PVA microfiber with the optimal diameter was identified using an optical microscope.

Acknowledgements

This project was primarily supported by the National Natural Science Foundation of China (Nos. 62375223, 62322510, and 61975166) and the Key Research and Development Program (Grant No. 2022YFA1404800). The authors thank the Analytical & Testing Centre of NPU for their assistance with material and device characterisation.

Author contributions

The manuscript was written with contributions from Y. M. and B. J. Y. M. conducted the experiments assisted by X. X. and Z. H. B. J., X. G., and J. Z. modified the manuscript.

Data availability

All data are available from the corresponding authors upon reasonable request.

Conflict of interest

The authors declare no competing interests.

Received: 10 October 2023 Revised: 12 November 2024 Accepted: 13 November 2024

Accepted article preview online: 14 November 2024

Published online: 27 December 2024

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