This is an electronic reprint of the original article.

This reprint may differ from the original in pagination and typographic detail.

Chen, Ke; Zhou, Xu; Cheng, Xu; Qiao, Ruixi; Cheng, Yi; Liu, Can; Xie, Yadian; Yu, Wentao; Yao, Fengrui; Sun, Zhipei; Wang, Feng; Liu, Kaihui; Liu, Zhongfan

Graphene photonic crystal fibre with strong and tunable light–matter interaction

Published in:
Nature Photonics

DOI:
[10.1038/s41566-019-0492-5](https://doi.org/10.1038/s41566-019-0492-5)

Published: 12/08/2019

Document Version
Peer reviewed version

Please cite the original version:

Chen, K., Zhou, X., Cheng, X., Qiao, R., Cheng, Y., Liu, C., Xie, Y., Yu, W., Yao, F., Sun, Z., Wang, F., Liu, K., & Liu, Z. (2019). Graphene photonic crystal fibre with strong and tunable light–matter interaction. *Nature Photonics*, 13, 754–759. <https://doi.org/10.1038/s41566-019-0492-5>

This material is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of the repository collections is not permitted, except that material may be duplicated by you for your research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered, whether for sale or otherwise to anyone who is not an authorised user.

Graphene Photonic Crystal Fibre with Strong and Tunable Light-Matter Interaction

Ke Chen^{1,2#}, Xu Zhou^{3#}, Xu Cheng^{3#}, Ruixi Qiao³, Yi Cheng^{1,4}, Can Liu³, Yadian Xie^{1,4}, Wentao Yu³,
Fengrui Yao³, Zhipei Sun⁵, Feng Wang⁶, Kaihui Liu^{3*}, Zhongfan Liu^{1,4*}

¹ Centre for Nanochemistry, Beijing Science and Engineering Centre for Nanocarbons, Beijing National Laboratory for Molecular Sciences, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

² Institute of Micro/Nano Photonic Materials and Applications, School of Physics and Electronics, Henan University, Kaifeng 475004, China

³ State Key Laboratory for Mesoscopic Physics, Academy for Advanced Interdisciplinary Studies, School of Physics, Peking University, Beijing 100871, China

⁴ Beijing Graphene Institute (BGI), Beijing 100095, China

⁵ Department of Electronics and Nanoengineering and QTF Centre of Excellence, Aalto University, FI-00076, Aalto, Finland

⁶ Department of Physics, University of California at Berkeley, Berkeley, CA 94720, USA

[#] These authors contributed equally to this work

* Correspondence: zfliu@pku.edu.cn; khliu@pku.edu.cn

The integration of photonic crystal fibre (PCF) with various functional materials has greatly expanded the application regimes of optical fibre¹⁻¹². The emergence of graphene excites new opportunities by combining with PCF, allowing for electrical tunability, broadband optical response and all-fibre integration ability¹³⁻¹⁸. However, the previous demonstrations are typically limited to the sample level of micron size, far behind the requirement of real applications for the metre-scale material level. Here, we demonstrate a new hybrid material of graphene photonic crystal fibre (Gr-PCF) with length up to half a metre by chemical vapour deposition method. The Gr-PCF shows strong light-matter interaction with $\sim 8 \text{ dB}\cdot\text{cm}^{-1}$ attenuation. In addition, the Gr-PCF-based electro-optic modulator demonstrates broadband response (1150 - 1600 nm) and large modulation depth ($\sim 20 \text{ dB}\cdot\text{cm}^{-1}$ at 1550 nm) under low gate voltage of ~ 2 volts. Our results could enable industrial-level graphene applications based on the Gr-PCF, and suggest an infusive platform of two-dimensional material-PCF.

Graphene is a promising material in photonic and optoelectronic applications due to its superior properties of high carrier mobility, broadband optical response and facile electrical tunability originating from its unique linear dispersion of massless Dirac fermions¹⁹⁻²⁸. Although the light-matter interaction in graphene normalized by its atomic thickness (0.34 nm) is quite strong, the measurable interaction is in fact quite weak (only $\sim 2.3\%$ light absorption)²⁹. To greatly enhance light-graphene interaction, many efforts have been devoted to combine graphene flakes with well-designed optical structures, such as gratings, waveguides and microcavities³⁰⁻³⁴, however, all those hybrid structures have still stayed at sample level of micron size, rather than material level of metre size, which limits their massive applications. Therefore, there exists great demand to develop new methods for massive production on graphene-based optical structures for material-level applications.

Optical fibre provides the highest-quality optical waveguide for information communication and photon manipulation, and it has been massively manufactured at kilometre length scale. PCF represents the most important advance of optical fibre in the last twenty years and possesses extremely rich functions beyond traditional optical fibre in the exciting applications of endlessly single-mode fibres, supercontinuum lasers, frequency combs, optical soliton propagation, high-power pulse delivery and so on¹⁻⁷. Especially, PCF with ingenious porous structure opens up the hard-won opportunity of filling various materials, ranging from gases, liquids, solids to liquid crystals, to expand its great new

functionalities in mode-locked fibre lasers, laser frequency conversion, surface plasmon generation, stimulated Raman scattering and in-fibre thermal- or electro-optic devices⁸⁻¹⁵. The rise of two-dimensional (2D) graphene naturally excites the keen interests in combining PCF with graphene. Such graphene-PCF complex can occupy several unique advantages: *(i)* the flexibility of graphene facilitates its tight attachment to the hole walls of PCF; *(ii)* the atomic thickness of graphene keeps the PCF structure and main optical function intact, and *(iii)* the distinct properties of graphene bring the unique functions that can't be realized by any other conventional materials. Indeed, great efforts have been delivered to fabricate graphene-optical fibre complex by transferring graphene flakes on side-polished or tapered normal optical fibres¹⁶⁻¹⁸, or filling them into the holes of PCFs¹³⁻¹⁵. However, all these attempts are only at sample level of micron length with small interaction area and harmful treating on fibre modes, and it is still lacking an efficient and nonharmful manufacture strategy for the massive production at metre-sized material level for graphene-PCF complex with large interaction area and intact structure yet.

In this work, we report the production of the new hybrid material of Gr-PCF with half-metre length by direct chemical vapour deposition (CVD) growth method, which was previously believed extremely challenging due to the lack of metal catalyst and the difficulties in gas flow control along the long micron-sized holes in silica PCF. Our success herein benefits from our extensive experience in the growth of graphene glass³⁵ and the well control of molecular gas flow in the confined space³⁶. With this new Gr-PCF material, we realized greatly enhanced light-matter interaction between graphene and core-guided light with $\sim 8 \text{ dB}\cdot\text{cm}^{-1}$ transmission attenuation. We also demonstrated the tunable light-matter interaction by electrically gating graphene through ionic liquid, with large modulation depth ($\sim 20 \text{ dB}\cdot\text{cm}^{-1}$ at 1550 nm) and broadband wavelength response (1150 - 1600 nm) under low gate voltage (~ 2 volts). And the fully enhanced and tunable light-matter interaction in Gr-PCF material indicates its great potentials in the all-fibre integration devices. Our results pave a new way for hybrid optical fibre manufacturing and suggest an exciting material platform of 2D materials-integrated fibre with unprecedented function tunability in both linear and nonlinear optics.

In our experiment, Gr-PCF was grown with methane (CH_4) as carbon feedstock flowing through the PCF's narrow holes ($\sim 4 \text{ }\mu\text{m}$ in diameter) under $\sim 1100 \text{ }^\circ\text{C}$ with controlled pressure (Fig. 1a). After the growth, the PCF can keep its structure intact which consists of a solid silica core and a surrounding

84 cladding region with a patterned array of holes (Fig. 1b), while graphene is grown on both the outer
85 surface and inner hole walls of PCF. The fully-covered graphene on the outer surface was
86 unambiguously evidenced by the Raman mapping (Fig. 1c and Supplementary Fig. 1). Representative
87 Raman spectrum (Fig. 1d) shows sharp G- and 2D-mode peaks, revealing the high quality of graphene
88 (The observable D peak mainly comes from the defective grain boundaries between graphene
89 domains)³⁷. The fully-covered graphene on the inner hole walls can be firstly indicated by the darker
90 optical contrast of Gr-PCF than bare PCF, due to the light absorption by graphene (Fig. 1e,f). Direct
91 evidence of graphene growth inside PCF can be given by the observation of tube-like graphene
92 frameworks that tightly attach on the hole walls and protrude out the holes when one breaks the Gr-PCF
93 (Fig. 1g and Supplementary Fig. 2). Furthermore, the inner graphene films can be directly obtained by
94 dissolving the fibre silica in hydrofluoric acid (the graphene film on the outer surface was first removed
95 by air-plasma treatment). The cylindroid graphene films from Gr-PCF collapse into ribbon films on
96 silicon substrate, with an average layer thickness of ~ 2.0 nm as measured by atomic force microscope
97 (AFM) (Fig. 1h,i). Here we note that the interlayer distance is relatively larger (estimated as 1.0 - 1.5 nm)
98 than its intrinsic interlayer distance (0.34 nm) in these collapsed ribbons, likely due to the wrinkles
99 formed during the etching treatment. The selected-area electron diffraction (SAED) in Fig. 1j
100 demonstrates the polycrystalline structure of the graphene film, as the selected-area aperture size (200
101 nm) is several times of graphene domain size (~ 50 nm). However, the high-resolution transmission
102 electron microscopy (HRTEM) image on individual graphene domain shows perfect graphene lattice
103 structure (Moiré pattern of bilayer as an example in Fig. 1k). More transmission electron microscopy
104 (TEM) characterizations reveal that the graphene thickness can be controlled between one to ten layers
105 by the growth time (Supplementary Fig. 3).

106 One great concern about the Gr-PCF growth is whether the graphene can be homogenously
107 distributed on the micron-sized hole walls along the long fibre, as gas flow in narrow space will have
108 huge viscous force. To clarify this point, we carried out control experiments with atmosphere pressure
109 chemical vapour deposition (APCVD, Fig. 2a) and low-pressure chemical vapour deposition (LPCVD,
110 pressure of 0.5 - 1.0 kPa, Fig. 2b). According to viscous flow model³⁸ (Supplementary Note 1), the mean
111 free path of carbon precursors (estimated as ~ 0.4 μm) is much shorter than the fibre hole diameter (~ 4
112 μm) under the atmosphere pressure in APCVD process. In this situation, the carbon precursor feeding is

limited by the mass transfer³⁶. According to experimental Raman data of graphene ribbons etched from the holes of Gr-PCF with ~8 cm length, the obvious variation of 2D- to G-mode Raman (intensity ratio I_{2D}/I_G , 0.6 - 2.1) and full width at half maximum of 2D-mode ($FWHM_{2D}$, 31 - 71 cm^{-1}) demonstrate the nonuniform thickness along the fibre axis (Fig. 2c,d, APCVD panels). This result is consistent with optical contrast observation that the fibre became darker along the gas flow direction (Supplementary Fig. 4, lower fibre). It means the graphene film thickness increases along the gas flow, originating from the increased active carbon species during the long-time thermal decomposition in the downstream positions. Whereas, in LPCVD process, the gas flow approaches a free molecular flow situation and the mass-diffusion process becomes negligible^{36,38}. In this case, the mean free path (estimated as $> 40 \mu m$) is much larger than hole size of PCF. Then elapse time (~15 s) of gaseous molecules going through the long holes of PCF in LPCVD process is much shorter than that in APCVD process (~175 s). It is facile to realize that the graphene films on the inner hole walls grow with uniform thickness along the fibre axis, as revealed by the Raman spectra with negligible fluctuation of I_{2D}/I_G ratio (~1.4) and $FWHM_{2D}$ (~48 cm^{-1}) (Fig. 2c,d, LPCVD panels), as well as the uniform optical imaging contrast along the whole fibre (Supplementary Fig. 4, upper fibre). Here we note that the intensity ratio of D- to G-mode Raman (I_D/I_G) has much larger value in LPCVD, revealing smaller graphene domain size³⁷, which originates from the lower carbon feedstocks, corresponding to the slower growth rate and the more nucleation centres under molecular flow. Using current furnace with heating zone of ~60 cm, we can readily grow Gr-PCF with uniform thickness and length up to 50 cm (Fig. 1e).

In principle, one would expect that the light-graphene interaction in Gr-PCF would be greatly enhanced as the atomic thickness of graphene wouldn't destroy the fundamental propagating mode. This assumption was checked by simulating the light electric field distribution of fundamental guiding mode with the full-vector finite element method³⁰. In the simulation, the graphene film directly interacts with light field by evanescent wave coupling at the hole walls adjacent to the fibre core (Fig. 3a). Similar to the distribution in bare PCF (Supplementary Fig. 5d), the light in Gr-PCF is mainly confined in the fibre core and about one tenth of the electric field to that at fibre core centre is interacting with graphene on the innermost hole walls (Fig. 3b). The light-graphene interaction can be first indicated by the 3% kink in the normalized radial electric field distribution, which originates from refractive index difference between graphene/silica and air. The significantly enhanced light-graphene interaction in Gr-PCF can be

quantitatively measured by the propagated light intensity evolution along the fibre. In a bare PCF of ~ 4 cm long, there is no observable attenuation ($< 0.01 \text{ dB}\cdot\text{cm}^{-1}$) at all (Fig. 3c, purple dots). However, in Gr-PCF, a strong attenuation of $8.3 \text{ dB}\cdot\text{cm}^{-1}$ is observed (Fig. 3c, cyan dots, fitted slope), in striking contrast with only 0.1 dB of suspended monolayer graphene. The attenuation coefficient value of this Gr-PCF is equivalent to average graphene layer number of ~ 1.5 (Fig. 3c, line and Supplementary Fig. 5i). Here the 0.5 layer comes from the partial second graphene layers grown on the first graphene layer film. The greatly enhanced light-graphene interaction in Gr-PCF can be qualitatively understood by the tremendous enlargement of effective interaction area and length during the multiple reflection of light propagation along the fibre axis (Fig. 3c, lower panel). It is worth noting that the light-graphene interaction strength can be tuned by the PCF geometries, such as the air-hole diameter and the hole pitch size (Supplementary Fig. 6).

One of the unique merits of 2D graphene is the unprecedented electrical tunability in light-matter interaction by shifting its Fermi level (E_F)^{21,26}. This tunability can be used to exploit the Gr-PCF as an in-line electro-optic modulator with intensity modulation in all-fibre communication networks (testing setup in Supplementary Fig. 7). Note that our Gr-PCF shows a stable and negligible loss ($< 0.1 \text{ dB}$) in coupling with single mode fibres. Here, we demonstrate an electro-optic modulator consisting of a short segment (0.5 - 1.5 cm) of Gr-PCF with ionic liquid (DEME-TFSI) filled inside the holes (Fig. 4a). The graphene on the hole walls of Gr-PCF connects electrically with an electrode on the outside graphene surface (the as-grown graphene films in the whole fibre are all connected). Ionic liquid is then fully filled in the fibre holes and contacts with another electrode. When gate voltage between graphene and ionic liquid is applied, electrical double layer (EDL) will form at graphene-ionic liquid interface and dope graphene efficiently under low gate voltage of several volts (Fig. 4b and Supplementary Fig. 8)^{26,39,40}. Further simulation reveals an additional advantage of ionic liquid filling that it can increase the light-graphene interaction from 5 to $24 \text{ dB}\cdot\text{cm}^{-1}$ for monolayer Gr-PCF by increasing the mode field area of core-guided light (Supplementary Fig. 5), as ionic liquid has a refractive index (1.42) close to that of the PCF material (silica, 1.44).

By electrically tuning graphene Fermi level via ionic liquid gating, the interband transition absorption can be tuned at “On” or “Off” state when E_F is smaller or larger than half photon energy of $\hbar\omega/2$, where ω and $\hbar\omega$ are the angular frequency and energy of a photon, respectively (Fig. 4c)^{21,30}. This

171 absorption-based electro-optic modulator operates at very low voltage (within 2 V) due to the efficient
172 electric double layer gating, and a broadband spectral response from 1150 to 1600 nm due to the linear
173 Dirac band structure of graphene (Fig. 4d). In particular, at the fibre-optic communication O- (1310 nm)
174 and C-wavelength bands (1550 nm), the modulation depths can respectively reach ~ 13 and ~ 20 dB $\cdot$ cm $^{-1}$
175 at gate voltage of -1.8 V (Fig. 4e). The relatively lower gating efficiency at positive gate voltage region
176 is attributed to the lower capacitance of our ionic liquid at electron doping side, which is consistent with
177 the electrical device measurement (Supplementary Fig. 8). The performance of our current modulator
178 can be further improved. Firstly, it has insertion loss of ~ 6 dB/cm in the “On” state, which can be much
179 lower in principle if one grows very high-quality monolayer graphene on the inside walls of PCF.
180 Secondly, it has slow switching speed of ~ 16 Hz (Supplementary Fig. 9) which can be improved (e.g.,
181 few 10s GHz^{17,31}) if one can achieve optimized structures, such as Gr/hBN/Gr-PCF⁴¹. Nevertheless, the
182 Gr-PCF modulator has high potential to be integrated with other optical devices in all-fibre system
183 where light can be synchronically transmitted, modulated and detected inside fibre link without the aid
184 of discrete devices in the future⁴².

185 In summary, we demonstrated an ingenious CVD route to achieve a new material of Gr-PCF. The
186 uniform and high-quality graphene on both the outer surface and inner hole walls of PCF with length up
187 to half a metre was realized by low pressure growth with controlled molecular flow. Such Gr-PCF
188 material exhibits a strong and tunable light-matter interaction and presents excellent performance as a
189 broadband electro-optic modulation under low gate voltage. As added convenient electrical tunability,
190 kept PCF waveguide mode intact and enhanced light-graphene interactions in both linear and nonlinear
191 optical regime, Gr-PCF enables the potential advent of novel fibre-optic devices such as
192 electrically-tunable mode-locked all-fibre lasers, gate-controllable wavelength-independent nonlinear
193 wavelength converters, tunable broadband polarizers and optical limiters in the near future. In addition,
194 our growth strategy can open up a new direction for massive production of other 2D crystals based
195 all-fibre devices, targeting to the next-generation optical fibres with various new functionalities.

196 **Online content**

197 Any methods, additional references, Nature Research reporting summaries, source data, statements of
198 data availability and associated accession codes are available at <https://doi.org/xxx/xxx>

199 Received: xx xx xxx; Accepted: xx xx xxx;

201 **References**

- 202 1 Russell, P. Photonic crystal fibers. *Science* **299**, 358-362 (2003).
- 203 2 Knight, J. C. Photonic crystal fibres. *Nature* **424**, 847-851 (2003).
- 204 3 Ouzounov, D. G. et al. Generation of megawatt optical solitons in hollow-core photonic band-gap
205 fibers. *Science* **301**, 1702-1704 (2003).
- 206 4 Bartels, R. A. et al. Generation of spatially coherent light at extreme ultraviolet wavelengths.
207 *Science* **297**, 376-378 (2002).
- 208 5 Couny, F., Benabid, F., Roberts, P. J., Light, P. S. & Raymer, M. G. Generation and photonic
209 guidance of multi-octave optical-frequency combs. *Science* **318**, 1118-1121 (2007).
- 210 6 Dudley, J. M. & Taylor, J. R. Ten years of nonlinear optics in photonic crystal fibre. *Nat. Photon.* **3**,
211 85-90 (2009).
- 212 7 Jiang, X. et al. Deep-ultraviolet to mid-infrared supercontinuum generated in solid-core ZBLAN
213 photonic crystal fibre. *Nat. Photon.* **9**, 133-139 (2015).
- 214 8 Benabid, F., Knight, J. C., Antonopoulos, G. & Russell, P. S. J. Stimulated Raman scattering in
215 hydrogen-filled hollow-core photonic crystal fiber. *Science* **298**, 399-402 (2002).
- 216 9 Abouraddy, A. F. et al. Towards multimaterial multifunctional fibres that see, hear, sense and
217 communicate. *Nat. Mater.* **6**, 336-347 (2007).
- 218 10 He, R. R. et al. Integration of gigahertz-bandwidth semiconductor devices inside microstructured
219 optical fibres. *Nat. Photon.* **6**, 174-179 (2012).
- 220 11 Kottig, F. et al. Mid-infrared dispersive wave generation in gas-filled photonic crystal fibre by
221 transient ionization-driven changes in dispersion. *Nat. Commun.* **8**, 813 (2017).
- 222 12 Rein, M. et al. Diode fibres for fabric-based optical communications. *Nature* **560**, 214-218 (2018).
- 223 13 Choi, S. Y. et al. Graphene-filled hollow optical fiber saturable absorber for efficient soliton fiber
224 laser mode-locking. *Opt. Express* **20**, 5652-5657 (2012).
- 225 14 Martinez, A. & Sun, Z. P. Nanotube and graphene saturable absorbers for fibre lasers. *Nat. Photon.*
226 **7**, 842-845 (2013).
- 227 15 Lin, Y.-H., Yang, C.-Y., Liou, J.-H., Yu, C.-P. & Lin, G.-R. Using graphene nano-particle embedded
228 in photonic crystal fiber for evanescent wave mode-locking of fiber laser. *Opt. Express* **21**,
229 16763-16776 (2013).
- 230 16 Bao, Q. L. et al. Broadband graphene polarizer. *Nat. Photon.* **5**, 411-415 (2011).
- 231 17 Li, W. et al. Ultrafast All-Optical Graphene Modulator. *Nano Lett.* **14**, 955-959 (2014).
- 232 18 Lee, E. J. et al. Active control of all-fibre graphene devices with electrical gating. *Nat. Commun.* **6**,
233 6851 (2015).
- 234 19 Zhang, Y. B., Tan, Y. W., Stormer, H. L. & Kim, P. Experimental observation of the quantum Hall
235 effect and Berry's phase in graphene. *Nature* **438**, 201-204 (2005).
- 236 20 Novoselov, K. S. et al. Two-dimensional gas of massless Dirac fermions in graphene. *Nature* **438**,
237 197-200 (2005).
- 238 21 Wang, F. et al. Gate-variable optical transitions in graphene. *Science* **320**, 206-209 (2008).
- 239 22 Xia, F. N., Mueller, T., Lin, Y. M., Valdes-Garcia, A. & Avouris, P. Ultrafast graphene photodetector.

240 *Nat. Nanotechnol.* **4**, 839-843 (2009).

241 23 Bonaccorso, F., Sun, Z., Hasan, T. & Ferrari, A. C. Graphene photonics and optoelectronics. *Nat.*
242 *Photon.* **4**, 611-622 (2010).

243 24 Grigorenko, A. N., Polini, M. & Novoselov, K. S. Graphene plasmonics. *Nat. Photon.* **6**, 749-758
244 (2012).

245 25 Gan, X. T. et al. Chip-integrated ultrafast graphene photodetector with high responsivity. *Nat.*
246 *Photon.* **7**, 883-887 (2013).

247 26 Polat, E. O. & Kocabas, C. Broadband Optical Modulators Based on Graphene Supercapacitors.
248 *Nano Lett.* **13**, 5851-5857 (2013).

249 27 Guo, Q. et al. Efficient electrical detection of mid-infrared graphene plasmons at room temperature.
250 *Nat. Mater.* **17**, 986-992 (2018).

251 28 Romagnoli, M. et al. Graphene-based integrated photonics for next-generation datacom and telecom.
252 *Nat. Rev. Mater.* **3**, 392-414 (2018).

253 29 Nair, R. R. et al. Fine structure constant defines visual transparency of graphene. *Science* **320**,
254 1308-1308 (2008).

255 30 Liu, M. et al. A graphene-based broadband optical modulator. *Nature* **474**, 64-67 (2011).

256 31 Phare, C. T., Lee, Y. H. D., Cardenas, J. & Lipson, M. Graphene electro-optic modulator with 30
257 GHz bandwidth. *Nat. Photon.* **9**, 511-514 (2015).

258 32 Lin, H. T. et al. Chalcogenide glass-on-graphene photonics. *Nat. Photon.* **11**, 798-805 (2017).

259 33 Sorianello, V. et al. Graphene-silicon phase modulators with gigahertz bandwidth. *Nat. Photon.*
260 **12**, 40-44 (2018).

261 34 Yao, B. C. et al. Gate-tunable frequency combs in graphene-nitride microresonators. *Nature* **558**,
262 410-414 (2018).

263 35 Sun, J. Y. et al. Graphene Glass from Direct CVD Routes: Production and Applications. *Adv. Mater.*
264 **28**, 10333-10339 (2016).

265 36 Wang, H. et al. Surface Monocrystallization of Copper Foil for Fast Growth of Large Single-Crystal
266 Graphene under Free Molecular Flow. *Adv. Mater.* **28**, 8968-8974 (2016).

267 37 Sato, K. et al. D-band Raman intensity of graphitic materials as a function of laser energy and
268 crystallite size. *Chem. Phys. Lett.* **427**, 117-121 (2006).

269 38 Knudsen, M. *The kinetic theory of gases* (Methuen, London, 1952).

270 39 Ye, J. T. et al. Liquid-gated interface superconductivity on an atomically flat film. *Nat. Mater.* **9**,
271 125-128 (2010).

272 40 Fujimoto, T. & Awaga, K. Electric-double-layer field-effect transistors with ionic liquids. *Phys.*
273 *Chem. Chem. Phys.* **15**, 8983-9006 (2013).

274 41 Yang, W. et al. Epitaxial growth of single-domain graphene on hexagonal boron nitride. *Nat. Mater.*
275 **12**, 792-797 (2013).

276 42 Yamashita, S. Nonlinear optics in carbon nanotube, graphene, and related 2D materials. *Appl. Phys.*
277 *Lett. Photon.* **4**, 034301 (2019).

278 **Acknowledgements**

279 This work was supported by National Key R&D Program of China (2016YFA0200103,
280 2016YFA0300903, 2016YFA0300804), Beijing Graphene Innovation Program (Z181100004818003,
281 Z161100002116028), NSFC (51432002, 51520105003, 51502077, 51522201, 11474006), Beijing
282 Municipal Science & Technology Commission (Z181100004218006), National Equipment Program of
283 China (ZDYZ2015-1), Postdoctoral Innovative Personnel Support Program (BX20180013), The Science
284 and Technology Development Project of Henan Province (182102210029), Zhongyuan Thousand
285 Talents Program of Henan Province, Young Talents Program of Henan University for support. Director,
286 Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division of the
287 U.S. Department of Energy under Contract No. DE-AC02-05-CH11231 (SP2 program), Academy of
288 Finland (276376, 295777, 312297, and 314810), Academy of Finland Flagship Programme (320167,
289 PREIN), the ERC (834742), and the European Union's Horizon 2020 research and innovation program
290 (820423, S2QUIP)

291 **Author contributions**

292 Z.L. and K.L. supervised the project. Z.L. and K.C. conceived the material growth. K.L. and X.Z.
293 conceived the optical measurement. K.C. and X.Z. carried out the material growth experiment and
294 optical device measurements. X.C. performed theoretical modelling. K.C., R.Q., Y.C., Y.X., X.Z., C.L.
295 and F.Y. conducted SEM, TEM, AFM and Raman characterizations. W.Y. suggested the optical
296 experiments. F.Y. programmed the measurement software. Z.S. and F.W. suggested the modulator. All
297 authors contributed to the scientific discussion and writing of the manuscript.

298 **Competing interests**

299 The authors declare no competing financial interests.

300 **Additional information**

301 **Supplementary information** is available is available for this paper at <https://doi.org/xxx/xxx>.

302 **Reprints and permissions information** is available at www.nature.com/reprints.

303 **Correspondence and requests for materials** should be addressed to Z.L. (for materials) and K.L. (for
304 optics).

305 **Publisher's note:** Springer Nature remains neutral with regard to jurisdictional claims in published
306 maps and institutional affiliations.

307 © The Author(s), under exclusive licence to Springer Nature Limited 2019

308 **Figure captions:**

309 **Fig. 1 | Growth and characterization of Gr-PCF.** **a**, Schematics of Gr-PCF grown by CVD method,
310 with graphene film on both outer surface and inner walls of PCF. **b**, SEM image of Gr-PCF end surface.
311 **c,d**, 2D-mode Raman intensity mapping (**c**) and Raman spectrum (**d**) of graphene at fibre end surface. **e,f**,
312 Optical reflection photograph (**e**) and transmission micrograph (**f**) of bare PCF and Gr-PCF. The optical
313 contrast is darker for Gr-PCF due to the light absorption by graphene. **g**, SEM image of a tube-like
314 graphene protruding out one hole of the fractured Gr-PCF. **h**, SEM image of a graphene ribbon (the
315 collapsed tube-like graphene grown on the hole wall) after dissolving the fibre silica. **i**, AFM image of a
316 graphene ribbon with wrinkles. The height of ~ 2.0 nm is obtained along the white dash line. **j,k**, SAED
317 (**j**) and HRTEM (**k**) images of the graphene ribbon.

318 **Fig. 2 | Controlled growth of uniform graphene film on the hole walls of PCF.** **a,b**, Schematics of
319 graphene growth on the walls of the micron-size holes of PCFs at atmosphere pressure (AP) and low
320 pressure (LP) CVD. **c**, Representative Raman spectra of graphene at different positions of graphene
321 ribbons along the gas flow under APCVD (upper panel) and LPCVD (lower panel) growth conditions.
322 The graphene ribbons are from the hole walls after etching away the fibre silica. **d**, The statistics of I_D/I_G ,
323 I_{2D}/I_G and the FWHM_{2D} of graphene Raman peak at different positions of graphene ribbons by APCVD
324 and LPCVD, where D, G and 2D stands for D-, G- and 2D-mode Raman peaks of graphene, respectively.

Fig. 3 | Strong light-matter interaction in Gr-PCF. **a**, The simulated light electric field distribution of the fundamental guiding mode at 1550 nm. The graphene is set on the hole wall shown in the profiles of Gr-PCF (low panel, yellow rectangle). **b**, The distribution of normalized electric field in Gr-PCF along horizontal radial direction (yellow horizontal line in (a)). The right panel shows the zoom-in of the dash square in left panel. The black arrow highlights the graphene position. **c**, Measured optical attenuation of light propagation in bare PCF (purple dots) and Gr-PCF (cyan dots) with different fibre lengths. The attenuation coefficient is fitted as $8.3 \text{ dB}\cdot\text{cm}^{-1}$ of the slope. The lower panel gives the schematic of light attenuation with multiple reflection during its propagating along Gr-PCF core. The error bar is the standard deviation from the measurement of 5 samples for each length grown at the same growth conditions.

Fig. 4 | Tunable light-matter interaction in Gr-PCF. **a**, Schematic of a Gr-PCF-based electro-optic modulator. The gate voltage between ionic liquid and graphene controls the light transmission through Gr-PCF. **b,c**, The working principle of Gr-PCF electro-optic modulator where electric double layer forms at interface between graphene (dark grey rectangle) and ionic liquid (blue area). The ionic liquid-gating tunes the graphene's Fermi level and switches on and off the optical absorption in graphene. When $E_F < \hbar\omega/2$ ($E_F > \hbar\omega/2$), graphene absorbs (doesn't absorb) light and the modulator is working at "Off" ("On") state for light transmission in the fibre. **d**, Two-dimensional mapping of transmission modulation (normalized by fibre length) of Gr-PCF modulator as a function of gate voltage and optical wavelength. **e**, The modulation curves at 1310 and 1550 nm show an unambiguous transition between "On" and "Off" state with large modulation depth.

Methods

Growth of Gr-PCFs. The PCFs (125 μm of cladding diameter and 8 μm of core diameter) were placed in the centre of a tube furnace (Thermo Linderberg). For APCVD process, CH_4 (10 sccm) was introduced as a carbon feedstock with Ar (100 sccm) and H_2 (50 sccm) at 1100 $^\circ\text{C}$ for hours under atmosphere pressure. For LPCVD process, CH_4 (50 sccm) was mixed with the H_2 (50 sccm) at 1100 $^\circ\text{C}$ for hours under pressure of 500 - 1000 Pa. After the growth, the as-grown sample was naturally cooled down in the protective gases of Ar and H_2 .

Characterization of Gr-PCFs. An optical microscope (Olympus BX51) was used to obtain the optical images of Gr-PCFs. SEM images were collected by FEI NovaTM Nano-SEM430 at 5 kV. Raman spectra and mappings were taken by WITec alpha 300R-confocal Raman imaging system equipped with a 532 nm laser. AFM pictures and data were performed in a Bruker Dimension Icon atomic force microscope. HRTEM and SAED experiments were performed in an aberration-corrected FEI Titan Themis G2-300 at 80 kV.

Numerical modelling. Numerical simulations were processed by the RF module of COMSOL's Multiphysics software and MATLAB software. The effective refractive index of fundamental guiding mode in Gr-PCFs was calculated by finite element method in COMSOL.

Device fabrication and modulation measurement. Ti/Au (5/100 nm) electrodes were deposited on graphene film by e-beam evaporation. The ionic liquid (DEME-TFSI, Sigma-Aldrich, CAS: 464927-84-2) was injected into holes of Gr-PCF with another Ti/Au electrode connection. The two ends of Gr-PCF were connected with two single-mode optical fibres (SMFs, Corning SMF-28e+) and the gap between fibres were filled with ionic liquid. The two SMFs were aligned in line with Gr-PCF by our home-built setup (Supplementary Fig. 6), where two optical microscopic observation in different directions and multi-axis piezo-stages ensured the accurate alignment. Keithley 2400 Source Meter provided the gate voltage. Supercontinuum laser (NKT Photonics Inc.) was coupled into SMF to provide broadband light. Modulated signal was sent into a spectrograph equipped with an infrared CCD (Princeton Instruments: Acton SpectraPro® SP-2300 and Pylon-IR 1024-1.7).

371 **Data availability**

372 The data that support the plots within this paper and other findings of this study are available from the
373 corresponding author upon reasonable request.

Fig.1

Fig.2

Fig.3

Fig.4