Black phosphorus polycarbonate polymer composite for pulsed fibre lasers

Diao Li^{a,b}, Antonio Esau Del Rio Castillo^c, Henri Jussila^a, Guojun Ye^{d,e}, Zhaoyu Ren^b, Jintao Bai^b, Xianhui Chen^{d,e,f}, Harri Lipsanen^a, Zhipei Sun^a, Francesco Bonaccorso^{c,1}

^aDepartment of Micro- and Nanosciences, Aalto University, P.O. Box 13500, FI-00076 Aalto, Finland

^bInstitute of Photonics and Photo-technology, Northwest University, Xi'an, 710069, China

^cIstituto Italiano di Tecnologia, Graphene Labs 16163, Genova, Italy

^dHefei National Laboratory for Physical Science at Microscale and Department of Physics, University of Science and Technology of China, Hefei, 230026, China

^eKey Laboratory of Strongly-coupled Quantum Matter Physics, University of Science and Technology of China, Chinese Academy of Sciences, Hefei, 230026, China

^fCollaborative Innovation Center of Advanced Microstructures, Nanjing, 210093, China

Abstract

Recently, the re-discovered black phosphorus (BP) has been extensively investigated for both electronic and photonic applications. However, the intrinsic instability of BP caused by moisture or oxygen reaction in ambient atmosphere has overshadowed its practical applications. Here, we present a liquid phase exfoliation-based approach for the production of few-layer BP (FL-BP) and the subsequent mixing with polycarbonate (PC) for the fabrication of a composite, which significantly reduces BP degradation by PC passivation. Experimentally, the functionalized PC few-layer BP (PC/FL-BP) composite shows environmental stability if compared with mechanically exfoliated BP flakes. We then use the PC/FL-BP composite as saturable absorber to study the nonlinear absorption property in a fibre laser at the 1.55 μm telecommunication wavelength. A Q-switched laser with pulse energy up to 25.2 nJ and pulse duration down to 1.65 μs is obtained at a low pump power of 71.7 mW. Our results can boost

¹ Email address: francesco.bonaccorso@iit.it; zhipei.sun@aalto.fi

further research and scalable photonic applications, where environmentally stable few-layer BP based devices are needed.

Keywords: Liquid phase exfoliation, few-layer black phosphorus, polycarbonate-black phosphorus composite, saturable absorber, passive Q-switching, fibre laser.

1. Introduction

Pulsed fibre lasers possess great advantages for various applications, if compared with pulsed solid-state lasers, such as telecommunication, sensing, spectroscopy, and medicine, due to their remarkable performance in terms of compactness, cost effectiveness, environmental insensitivity and effective thermal dissipation [1, 2]. To date, the state-of-the-art pulsed laser technology is strongly dependent on the development of saturable absorbers (SAs), which are nonlinear optical components that enable pulse generation [3]. Currently, semiconductor saturable absorber mirrors (SESAMs) are dominating the SA market due to their excellent saturable absorption performance [3, 4, 5]. However, the complex fabrication and packaging technology of SESAMs make them expensive devices [6, 7]. Furthermore, SESAMs typically have only a few tens of nanometre operation bandwidth in the near-infrared region [5, 8]. Thus, SAs based on new materials and novel techniques offering complementary performance are highly desirable.

Recently, graphene [9, 10, 11, 12, 13, 14] was experimentally identified as a promising SA for broadband ultrafast pulse generation in various laser systems (e.g., fibre [9, 10, 11, 12, 13, 14, 15, 16], waveguide [17], solid-state [18, 19], semiconductor [20] lasers) because of its unique properties and performance, such as fast recovery time [15], broad operation bandwidth [21, 22, 23], easy and cost-effective fabrication and integration [24]. Nevertheless, the weak optical absorption in graphene ($\sim 2.3\%$ for monolayer [25, 26]) limits the modulation depth, which is a key parameter for ultrafast fibre lasers. Other two-dimensional (2D) crystals, such as transition metal di-

chalcogenides (TMDs) (including MoS₂ [27, 28, 29], MoSe₂ [30], WS₂ [30]) have also been explored as SAs. Differently from graphene, these inorganic 2D crystals typically exhibit large band gap in their monolayer form (i.e., ~1.8 eV for MoS₂, 1.7 eV for WSe₂, 2.1 eV for WS₂), which are not suitable for fibre laser technology, generally operating in the near- and mid-infrared region [27, 29, 12]. Most recently, black phosphorus (BP), a layered crystal, has attracted great attention in electronics and photonics [12, 31, 32, 33, 34]. In contrast with graphene and many layered TMDs, BP presents a thickness dependent band gap tunability from 0.3 eV (in bulk) to ~1.5 eV (in monolayer) [12, 35, 36, 37], which could bridge the gap between the zero band gap of graphene and the large band gap of layered TMDs [21]. Moreover, BP always shows direct band gap either in bulk or layered form [32], enabling its application as an ideal semiconductor for electronics and photonics [31, 38]. Inspired from graphene and other 2D crystals, the optical property of BP also attracts extensive interests [39, 40, 41, 42, 43, 44]. Up to date, BP has been successfully utilized in pulsed laser generation ranging from near infrared (~1 μm) to mid-infrared (~2.8 μm) [39, 40, 41, 42, 43, 44], demonstrating its broadband nonlinear optical responsivity.

Noteworthy, most of the demonstrated BP photonic devices (including those used for ultrafast lasers) [39, 40, 41, 44] were based on BP produced by mechanical cleavage and used in ambient atmosphere. This determines a critical issue on the optical instability induced by the potential layer-by-layer etching derived from moisture [45] or oxidation reaction [46] within few layers BP (FL-BP). Moreover, the material erosion has been considered a critical point that could cause significant performance degradation in BP based optoelectronic devices [45, 46, 47], which are generally used in ambient conditions. To overcome this issue, various optimizing strategies to protect and shield BP have been proposed [48, 49, 50, 51, 52]. For example, coating inert Al₂O₃ layers on BP by atomic layer deposition (ALD) method was studied to reduce the amount of the atmosphere/BP reactions by surface passivation [48, 49]. Atomically-thick hexagonal boron nitride (*h*-BN) layer and polymethyl methacrylate (PMMA) film were also introduced to preserve the

pristine performance of BP flakes [50, 51, 52] by encapsulation. However, ALD covering is not suitable for monolayer or FL-BP with low stability, because the ALD process may lead to rapid oxidation of the BP flakes [46, 53]. Moreover, the fabrication of *h*-BN films and their use for BP encapsulation require rigorous parametric and environmental control [50, 54], which significantly increases both cost and technological complexity. Overall, although these passivation methods are well implemented in BP devices produced by mechanical exfoliation, they have drawbacks concerning large scale production and lack of flexibility due to the need of the transfer process to arbitrary substrates.

The weak layer-by-layer van der Waals stacking provides the possibility to produce FL-BP by exfoliation method [55]. In recent studies, it has been demonstrated that liquid phase exfoliation (LPE) is a scalable and cost-effective method for the production of FL-BP [56, 57, 58, 59], opening the way to new applications based on functional polymer/FL-BP composites or functional inks [56, 59]. In this work, we exploited LPE for the BP preparation and the subsequent realization of functional FL-BP composite blending with polycarbonate. Polycarbonate is selected because of its broad optical transparency in the visible and near-infrared range, a property previously exploited for the realization of composites for ultrafast lasers [60]. A long term optical absorption test in ambient atmosphere clearly shows that the PC/FL-BP composite is more stable than the mechanically exfoliated BP flakes. We then integrate the PC/FL-BP composite into a fibre laser at 1.55 μm , the telecommunication wavelength, for Q-switching operation. Large energy pulse with pulse energy up to 25.2 nJ and pulse duration down to 1.65 μs is generated at the maximum pump power of 71.7 mW. These results demonstrate the effective nonlinear optical property of our functional PC/FL-BP composite, paving the way for the practical implementation of FL-BP in photonic and optoelectronic applications.

2. Black phosphorus polymer composite fabrication

2.1. Selection of solvents for the black phosphorus exfoliation

By using the approximation $\gamma = E - T \times S$ (where γ is the surface tension, E is the solvent surface energy, T is the absolute temperature, and S is the solvent surface entropy,

which generally takes a value of $0.1 \text{ mJm}^{-2}\text{K}^{-1}$ [61, 62]), we can select the solvent by estimating the surface tension (γ) to exfoliate bulk BP and get a stable dispersion of FL-BP. In this experiment, the surface energy (E) of BP is $\sim 60 \text{ mJm}^{-2}$ [63]. Therefore, a solvent with a surface tension (γ) of $\sim 30 \text{ mNm}^{-1}$ is needed, which is deduced by replacing the surface energy of BP in the approximate equation aforementioned at room temperature (i.e., 300 K). N-Cyclohexyl-2-pyrrolidone (CHP), having a surface tension (γ) of 37 mNm^{-1} [64] is then considered an appropriate solvent for the LPE process of BP, starting from the exfoliation of powder-like BP and the preparation of FL-BP dispersion [56].

2.2. Black phosphorus exfoliation process

100 mg of bulk BP crystals (centimetre size, from Smart Elements) are crushed, using a mortar inside a glovebox, to reduce size and get a powder-like sample. Before performing the LPE process, the powder-like BP is dispersed in 100 mL of CHP (Sigma Aldrich, boiling point: 284°C) and dispersed by using an ultrasonic bath for 6 hours. The ultra-sonicated BP in CHP solution is then centrifuged at $\sim 560 \text{ g}$ in a Sigma 3-16KL centrifuge for 180 minutes, exploiting the sedimentation-based separation (SBS) process [11, 56, 61, 65, 66, 67, 68], to separate thick and/or un-exfoliated BP flakes from the thinner ones.

2.3. Few-layer BP polycarbonate composite

For the realization of the BP-based composite, the LPE BP flakes in dispersion should then mix with polycarbonate. To obtain a completely dry composite, the blending with BP flakes and polycarbonate requires the removal of the solvent [11, 60, 69, 70, 71]. However, the CHP removal by direct evaporation is unfeasible in our process because the boiling point of CHP (284°C) determines polycarbonate degradation (melting point 155°C , glass transition temperature: 147°C [72]). Contrary, chloroform has a low boiling point (61°C) and is also a solvent able to disperse polycarbonate [73]. Unfortunately, it is not possible to exfoliate bulk BP directly in chloroform, due to the lack of the required physical-chemical properties, such as γ , as discussed in

aforementioned paragraph [67]. Thus, we carried out a solvent exchange process by using centrifugation [68, 74] to remove the CHP and re-disperse the exfoliated BP flakes in chloroform. In the solvent exchange process, 20 mL of chloroform (from Sigma Aldrich) are added to the BP-based CHP dispersion and centrifuged at 560 g, 90% of the supernatant is discarded and the precipitate is re-suspended in 20 mL of chloroform. This CHP removal is repeated 4 times to optimize the process. Finally, the precipitate is re-suspended in 5 mL of chloroform and dispersed by using an ultrasonic bath for 5 minutes. The entire solvent exchange process is carried out under inert atmosphere. 100 mg of polycarbonate pellets (Molecular weight: 45 000, from Fisher) are dispersed in 10 mL of chloroform via stirring process. Subsequently, 1 mL of the BP-based chloroform dispersion and 2 mL of polycarbonate in chloroform are mixed. After the evaporation of solvent at room temperature, the experimentally available PC-BP composite is obtained. This procedure has several advantages with respect to the exfoliation of 2D crystals in the target solvent [66, 67, 68]. First, it allows the exfoliation of the layered materials (i.e., BP) in the solvent with the required physical-chemical properties (e.g., γ and viscosity), obtaining a dispersion with high quality (e.g., both by weight and single layer percentage) [24]. Second, it allows changing the solvent on-demand, according to the target application, i.e., change to a non-toxic solvent for electronic applications [68] or organic solvents for polymer dispersion [75]. Third, it is also possible to tune the concentration of the obtained dispersion [76], according to the final application.

3. Material characterization

3.1. Black phosphorus and its polymer composite characterization

The concentration of the exfoliated BP in CHP and exchanged in chloroform is determined by optical absorption spectroscopy (OAS) (as shown in Fig. 1a), which is carried out with a Cary Varian 5000 UV-VIS spectrophotometer. To facilitate the OAS measurements, the BP dispersion in CHP and in chloroform are diluted 1:10 and 1:50 in their respective solvents. The concentration of BP flakes in dispersion is then determined from the OAS measurements at the wavelength of 684 nm [77]. By using the formula $A = \alpha lc$, where α [$\text{Lg}^{-1} \text{m}^{-1}$] is the absorption coefficient, with $\alpha \sim 2767$

$Lg^{-1}m^{-1}$ [77], l [m] is the light path length and c [gL^{-1}] is the concentration of dispersed BP flakes, the concentration of the exfoliated BP in CHP and exchanged in chloroform is calculated to be 0.12 gL^{-1} and 1.8 gL^{-1} , respectively.

Raman spectroscopy is a powerful tool to investigate the physical-chemical properties of the exfoliated BP flakes, such as thickness [56, 78, 79], strain or stress [80, 81, 82], and oxidation [83]. In order to carry out the measurement, the as-prepared dispersions of BP in CHP and chloroform are drop-cast onto a Si wafer with 300 nm thermally grown SiO_2 (LDB Technologies Ltd.) and dried in vacuum. Raman measurements of BP flakes are collected by a Renishaw inVia confocal Raman microscope using an excitation wavelength of 532 nm (2.33 eV) with a 50 $\times$ objective, and an incident power of ~ 1 mW on the samples. For each sample we collected 10 spectra for statistical analysis. The Raman spectra of BP consist of three peaks, originating from an out-of-plane mode (A^1 , located at 362 cm^{-1}) and two in-plane modes (A^2 and B_{2g} , located at $\sim 465\text{ cm}^{-1}$ and $\sim 440\text{ cm}^{-1}$), [56, 84] as schematically depicted in Figs. 1b and 1c, respectively. We carried out Raman analysis for the bulk BP, the exfoliated BP in CHP and the BP flakes exchanged in chloroform (see Fig. 1b). Raman analysis confirms that the exfoliation process of the bulk BP does not damage the crystal structure of BP layers [56, 78, 79].

The as-prepared dispersion in CHP as well as the one after solvent exchange in chloroform are subsequently characterized by transmission electron microscopy (TEM) (JOEL JEM 1011). For the analysis, the BP dispersions in CHP and chloroform are diluted 1:10 in their respective solvents and successively dropped onto holey carbon 200 mesh grids and dried in vacuum overnight. The measurements are carried out with an acceleration voltage of 100 kV. The TEM images of BP in CHP and in chloroform are shown in Figs. 1d and 1e, respectively. **The lateral size of the BP flakes is quite heterogeneous, ranging from 0.1 to 1.5 μm and did not change during the solvent exchange process, as shown in the histogram in Fig. 1f. From the TEM images we can estimate a thickness of ~ 15 layers, demonstrating the presence of FL-BP. Moreover, no degradation**

or aggregation of the FL-BP flakes is observed after the solvent exchange process in chloroform.

The PC/FL-BP composite is finally dried at room temperature to form a film with thickness of ~ 110 μm . The FL-BP flakes in chloroform, the polycarbonate and the PC/FL-BP composite film are also characterized by means of Raman spectroscopy, respectively. Figure 2 shows the spectra of the FL-BP in chloroform (blue curve), the polycarbonate (grey curve) and the PC/FL-BP composite (red curve). There are no significant changes in the Raman features of the aforementioned samples, indicating that no structural changes occur following the polymer composite preparation protocol. The shift of ~ 2 cm^{-1} of the B_{2g} and A^2_g peaks, is possibly due to the strain effect in the flakes induced by the processes of solvent evaporation and drying of the polycarbonate matrix [80, 81, 82].

3.2. Stability characterization of mechanically exfoliated BP flakes and PC/FL-BP composite

To compare the performance degradation of the mechanically exfoliated BP flakes and our PC/FL-BP composites in ambient atmosphere, a long term optical stability experiment was implemented and shown in Fig. 3. A multi-layer BP thin film mechanically exfoliated from a bulk BP flake operating as a reference sample was transferred on the end facet of a fibre connector (see Figs. 3b and 3c) by a micro-mechanical transfer platform with the help of an optical microscope [40, 53]. The thickness of the mechanically exfoliated BP flake is ~ 70 nm, measured by atomic force microscopy (AFM). Then, we exposed the transferred BP flake in ambient atmosphere at room temperature to monitor the optical transmission variation by injecting a 10 mW amplified spontaneous emission (ASE) laser at the 1.55 μm telecommunication band. As shown in the blue triangle curve of Fig. 3a, the optical transmittance of the mechanically exfoliated BP exhibits a rapid decrease of $\sim 9\%$ in the first 120 hours operation (i.e., from 60.7% to 51.5%). Hereafter, the optical transmittance decreases with an approximately linear rate of 0.6% per day. By carrying out the measurement up to 336 hours, the optical

transmittance reached a value of 46.3%, which represents a decrease as large as ~15% with respect to the initial transmission value. Worth noting, the transmittance decrease trend clearly indicates that this reduction would still continue after the 336-hour measurement, thereby, raising a question on the long-term performance of mechanically exfoliated BP-based photonic devices. Figures 3b and 3c illustrate the comparison of the BP degradation associated with the transmission measurement through the images taken by an optical microscope. A noticeable colour change is detected on the BP film at the fibre core, marked by the red solid circles in both figures. The bright cyan colour is probably induced by the oxidation reaction in air with the help of thermal-excitation of the photons [46]. These results experimentally confirm the weak resistance of mechanically exfoliated BP flakes under operation in ambient conditions.

We then transfer the functionalized PC/FL-BP composite on the surface of a new fibre connector, in order to investigate its stability at ambient atmosphere. The long term optical stability measurement of our PC/FL-BP composite was implemented and shown in Fig. 3a (red triangle curve). The optical transmittance, which is 63% at the beginning of the experiment, slightly increased ~2% after 200 hours, achieving a constant value of 65% afterward. This transmission variation is probably caused by the inconspicuous thermal distortion of polycarbonate in the composite [85]. Figures 3d and 3e show the morphology, as a comparison, before and after the optical transmission measurement of our PC/FL-BP composite. There is no noticeable surface damage observed in the PC/FL-BP composite film area illuminated by the optical beam. These results further confirm the remarkable stability of the as-prepared LPE-based PC/FL-BP composite.

4. PC/FL-BP composite for pulsed fibre laser application

4.1. Laser setup

We then tested our PC/FL-BP composite for optical pulse generation in an all-fibre laser. The laser setup with a fibre integrated PC/FL-BP composite SA is schematically

illustrated in Fig. 4. A segment of ~ 0.7 m Erbium doped fibre (EDF) was used to provide the gain at $1.55 \mu\text{m}$ telecommunication band, which was pumped by a 980 nm laser diode (LD) via a fused wavelength division multiplexer (WDM). To suppress the unidirectional propagation of the resonant light in the laser cavity, a polarization independent optical isolator was utilized. A polarization controller was used to adjust the polarization and birefringence in the laser cavity. The intra-cavity laser was extracted out from a 10/90 output coupler through the 10% port. All passive fibre employed in the laser cavity is SMF-28 (Corning). The full length of the laser cavity is ~ 10.7 m. To characterize the pulsed laser performance, we used an optical spectrum analyser (Anristu, MS9740A) to measure the output spectrum, an oscilloscope connected with an ultrafast photodetector to visualize the pulse train, and a power meter (Ophir, Nova II) to measure the output power.

4.2. Pulsed laser results and discussion

Before inserting the integrated PC/FL-BP composite SA in the laser cavity, we first evaluated the laser operation as a function of the pump power.

The output light shows only continuous wave performance, with no sign of Q-switching operation. After that, the PC/FL-BP composite integrated device was inserted in the laser cavity. Continuous wave laser oscillation started at the pump power of 7.5 mW. Q-switched output was observed at the pump power of 21.2 mW. The lasing and Q-switching thresholds are comparable to previously demonstrated Q-switched lasers wherein mechanically-exfoliated BP SAs are used [40]. Further increasing the pump power, the laser operated at stable Q-switching until the pump power achieved 71.8 mW. At a pump power higher than 71.8 mW, the output pulses became unstable and eventually disappeared, most probably due to the over-saturation of the SA at high pump power [39]. Figure 5 illustrates the laser output performance. A typical Q-switched pulse train is shown in Fig. 5a. The output repetition rate is 70.4 kHz, corresponding to a $14.2 \mu\text{s}$ adjacent pulse interval. Figure 5b shows a single pulse envelope that is extracted from the pulse train

within a time range of 10 μ s. The output pulse presents a symmetric edge with pulse duration down to 1.65 μ s. The inset of Fig. 5b plots the output spectrum of the pulsed laser at the pump power of 71.7 mW, in which the lasing wavelength is centred at 1531.2 nm with a full width at half maximum (FWHM) of 4.8 nm.

A typical characteristic of Q-switched lasers is the dependence on the pump power of both the output repetition rate and pulse duration. This can be explained as follow: when the pump power increases, the laser will provide more gain to saturate the SAs, thus the repetition rate increases and the pulse duration reduces. Figure 5c shows the repetition rate (red spheres) and pulse duration (blue spheres) as a function of the pump power, respectively. The repetition rate increases approximately linearly from 35.7 to 70.6 kHz, and the pulse duration reduces from 6.2 to 1.65 μ s, when the pump power varies between 21.2 to 71.7 mW. In contrast with the mode-locked lasers, Q-switched lasers generally output larger pulse energy (> 1 nJ) and longer pulses (from μ s to ns in a kHz repetition rate)[40, 86], which are more relevant for applications where optical pulses with large energy are needed. Figure 5d depicts the output power and the corresponding pulse energy as a function of the pump power, respectively. The output power increases linearly with the pump power in either continuous wave operation (pump power less than 21.2 mW) or Q-switching regime (pump power larger than 21.2 mW). The maximum output power and pulse energy under Q-switching operation are 1.78 mW and 25.2 nJ, when the pump power rises up to 71.7 mW, showing the performance comparable with the experimental results obtained with graphene [87] and other TMDs based SAs [88]. These results confirm the excellent saturable absorption property of our PC/FL-BP composite, which can be further used for ultrafast pulse generation and other nonlinear photonic applications, such as all-optical switches.

5. Conclusions

In conclusion, we have proposed a simple, cost-effective and industrially relevant method to synthesize BP through the combination of LPE and a solvent exchange process. The chemical stability of FL-BP in ambient conditions was significantly enhanced after the passivation with the polycarbonate, an inert material with optical transparency from visible

to infrared region. The fabricated PC/FL-BP composite was subsequently used as a SA for large energy pulse generation at 1.55 μm telecommunication wavelength. A Q-switched laser with output repetition rate, pulse duration and pulse energy ranging from 35.7 to 70.6 kHz, 6.2 to 1.65 μs and 8.7 to 25.2 nJ was demonstrated. Our results provide an alternative solution to manage the chemical degradation of BP flakes in ambient conditions, which opens perspective for the future applications of BP based devices in photonics and (opto)electronics.

Acknowledgements

The authors acknowledge funding from the European Union's Seventh Framework Programme (REA grant agreement No. 631610) and Graphene Flagship (contract number CNECT-ICT-604391), Teknologiateollisuus TT-100, Academy of Finland (No. 276376, 284548), Tekes (OPEC), Nokia foundation, International Science and Technology Cooperation Project (No. 2014DFR10780, China), the National Science Foundation for Young Scholars of China (No. 61505162), the Foundation of the Education Committee of Shaanxi Province (No. 14JK1756, China), China Scholarship Council and Northwest University Cross-discipline Fund for Postgraduate Students (No. YZZ13027). We also acknowledge the provision of technical facilities of the Micronova, Nanofabrication Centre of Aalto University.

References

- [1] F. Dausinger, F. Lichtner, H. Lubatschowski, Femtosecond technology for technical and medical applications, Springer Science (2004).
- [2] M. Fermann, A. Galvanauskas, G. Sucha, Ultrafast lasers: technology and applications, CRC Press 80 (2002).
- [3] U. Keller, Recent developments in compact ultrafast lasers, Nature 424 (6950) (2003) 831-838.

- [4] O. Okhotnikov, A. Grudinin, M. Pessa, Ultra-fast fibre laser systems based on sesam technology: new horizons and applications, *New J. Phys.* 6 (1) (2004) 177.
- [5] U. Keller, K. J. Weingarten, F. X. Kartner, D. Kopf, B. Braun, I. D. Jung, R. Fluck, C. Honninger, N. Matuschek, J. A. der Au, Semiconductor saturable absorber mirrors (SESAM's) for femtosecond to nanosecond pulse generation in solid-state lasers, *IEEE J. Sel. Top. Quantum Electron.* 2 (3) (1996) 435-453.
- [6] M. Haiml, U. Siegner, F. M. Genoud, U. Keller, M. Luysberg, R. Lutz, P. Specht, E. Weber, Optical nonlinearity in low-temperature-grown GaAs: Microscopic limitations and optimization strategies, *Appl. Phys. Lett.* 74 (21) (1999) 3134-3136.
- [7] F. Wang, A. Rozhin, V. Scardaci, Z. Sun, F. Hennrich, I. White, W. I. Milne, A. C. Ferrari, Wideband-tuneable, nanotube mode-locked, fibre laser, *Nat. Nanotechnol.* 3 (12) (2008) 738-742.
- [8] U. Keller, *Advances in all-solid-state ultrafast lasers*, Springer Ser. Chem. Phys. 62 (1996) 3-5.
- [9] T. Hasan, Z. Sun, F. Wang, F. Bonaccorso, P. H. Tan, A. G. Rozhin, A. C. Ferrari, Nanotube-polymer composites for ultrafast photonics, *Adv. Mater.* 21 (38-39) (2009) 3874-3899.
- [10] Q. Bao, H. Zhang, Y. Wang, Z. Ni, Y. Yan, Z. X. Shen, K. P. Loh, D. Y. Tang, Atomic-layer graphene as a saturable absorber for ultrafast pulsed lasers, *Adv. Funct. Mater.* 19 (19) (2009) 3077-3083.
- [11] Z. Sun, T. Hasan, F. Torrisi, D. Popa, G. Privitera, F. Wang, F. Bonaccorso, D. M. Basko, A. C. Ferrari, Graphene mode-locked ultrafast laser, *ACS Nano* 4 (2010) 803-810.
- [12] Z. Sun, A. Martinez, F. Wang, Optical modulators with two-dimensional layered materials, *Nat. Photonics* DOI: 10.1038/NPHOTON.2016.15 (2016).
- [13] S. Yamashita, A tutorial on nonlinear photonic applications of carbon nanotube and graphene, *Lightwave Technol.* 30 (4) (2012) 427-447.
- [14] A. Martinez, Z. Sun, Nanotube and graphene saturable absorbers for fibre lasers, *Nat. Photonics* 7 (2013) 842-845.

- [15] D. Popa, Z. Sun, F. Torrisi, T. Hasan, F. Wang, A. C. Ferrari, Sub 200 fs pulse generation from a graphene mode-locked fibre laser, *Appl. Phys. Lett.* 97 (20) (2010) 203106.
- [16] J. Sotor, G. Sobon, K. M. Abramski, Scalar soliton generation in all-polarization-maintaining, graphene mode-locked fibre laser, *Opt. Lett.* 37 (11) (2012) 2166-2168.
- [17] R. Mary, G. Brown, S. J. Beecher, F. Torrisi, S. Milana, D. Popa, T. Hasan, Z. Sun, E. Lidorikis, S. Ohara, A. C. Ferrari, A. K. Kar, 1.5 GHz picosecond pulse generation from a monolithic waveguide laser with a graphene-film saturable output coupler, *Opt. Express* 21 (2013) 7943-7950, 2013.
- [18] W. D. Tan, C. Y. Su, R. J. Knize, G. Q. Xie, L. J. Li, D. Y. Tang, Mode locking of ceramic Nd:yttrium aluminum garnet with graphene as a saturable absorber, *Appl. Phys. Lett.* 96 (2010) 031106.
- [19] A. A. Lagatsky, Z. Sun, T. S. Kulmala, R. S. Sundaram, S. Milana, F. Torrisi, O. L. Antipov, Y. Lee, J. H. Ahn, C. T. A. Brown, W. Sibbett, A. C. Ferrari, 2 μm Solid-state laser mode-locked by single-layer graphene, *Appl. Phys. Lett.* 102 (2013) 013113.
- [20] C. A. Zaugg, A. Klenner, M. Mangold, A. S. Mayer, S. M. Link, F. Emaury, M. Golling, E. Gini, C. J. Saraceno, B. W. Tilma, U. Keller, Gigahertz self-referenceable frequency comb from a semiconductor disk laser, *Opt. Express* 22 (2014) 16445-16455.
- [21] K. S. Novoselov, V. I. Fal'ko, L. Colombo, P. R. Gellert, M. G. Schwab, K. Kim, A roadmap for graphene, *Nature* 490 (2012) 192-200.
- [22] Z. Sun, D. Popa, T. Hasan, F. Torrisi, F. Wang, E. J. R. Kelleher, J. C. Travers, V. Nicolosi, A. C. Ferrari, A stable, wideband tunable, near transform-limited, graphene-mode-locked, ultrafast laser, *Nano Res.* 3 (9) (2010) 653-660.
- [23] B. Fu, Y. Hua, X. Xiao, H. Zhu, Z. Sun, C. Yang, Broadband graphene saturable absorber for pulsed fibre lasers at 1, 1.5 and 2 μm , *IEEE J. Sel. Top. Quantum Electron.* 20 (2014), 1100705.

- [24] F. Bonaccorso, A. Lombardo, T. Hasan, Z. Sun, L. Colombo, A. C. Ferrari, Production and processing of graphene and 2d crystals, *Mater. Today* 15 (12) (2012) 564-589.
- [25] R. R. Nair, P. Blake, A. N. Grigorenko, K. S. Novoselov, T. J. Booth, T. Stauber, N. M. R. Peres, A. K. Geim, Fine structure constant defines visual transparency of graphene, *Science* 320 (5881) (2008) 1308-1308.
- [26] K. Mak, M. Y. Sfeir, Y. Wu, C. H. Lui, J. A. Misewich, T. F. Heinz, Measurement of the optical conductivity of graphene, *Phys. Rev. Lett.* 101 (19) (2008) 196405.
- [27] F. Bonaccorso, Z. Sun, Solution processing of graphene, topological insulators and other 2d crystals for ultrafast photonics, *Opt. Mater. Express* 4 (1) (2014) 63-78.
- [28] H. Zhang, S. B. Lu, J. Zheng, J. Du, S. C. Wen, D. Y. Tang, K. P. Loh, Molybdenum disulfide (MoS_2) as a broadband saturable absorber for ultra-fast photonics, *Opt. Express* 22 (6) (2014) 7249-7260.
- [29] R. I. Woodward, R. C. T. Howe, G. Hu, F. Torrisi, M. Zhang, T. Hasan, E. J. R. Kelleher, Few-layer MoS_2 saturable absorbers for short-pulse laser technology: current status and future perspectives, *Photonics Res.* 3 (2) (2015) A30-A42.
- [30] Z. Luo, D. Wu, B. Xu, H. Xu, Z. Cai, J. Peng, J. Weng, S. Xu, C. Zhu, F. Wang, Z. Sun, H. Zhang, Two-dimensional materials saturable absorbers: Towards compact visible-wavelength all-fibre pulsed lasers, *Nanoscale* 8 (2016) 1066-1072.
- [31] L. Li, Y. Yu, G. J. Ye, Q. Ge, X. Ou, H. Wu, D. Feng, X. H. Chen, Y. Zhang, Black phosphorus field-effect transistors, *Nat. Nanotechnol.* 9 (2014) 372-377.
- [32] F. Xia, H. Wang, Y. Jia, Rediscovering black phosphorus as an anisotropic layered material for optoelectronics and electronics, *Nat. Commun.* 5 (2014) 4458.
- [33] X. Ling, H. Wang, S. Huang, F. Xia, M. Dresselhaus, The renaissance of black phosphorus, *Proc. Natl. Acad. Sci.* 112 (2015) 4523-4530.
- [34] F. Xia, H. Wang, D. Xiao, M. Dubey, A. Ramasubramaniam, Two-dimensional material nanophotonics, *Nat. Photonics* 8 (2014) 899-907.

- [35] T. Low, A. S. Rodin, A. Carvalho, Y. Jiang, H. Wang, F. Xia, A. H. C Neto, Tunable optical properties of multilayer black phosphorus thin films, *Phys. Rev. B* 90 (7) (2014) 075434.
- [36] S. Das, W. Zhang, M. Demarteau, A. Hoffmann, M. Dubey, A. Roelofs, Tunable transport gap in phosphorene, *Nano Lett.* 14 (10) (2014) 5733-5739.
- [37] V. Tran, R. Soklaski, Y. Liang, L. Yang, Layer-controlled band gap and anisotropic excitons in few-layer black phosphorus, *Phys. Rev. B* 89 (23) (2014) 235319.
- [38] M. Buscema, D. J. Groenendijk, S. I. Blanter, G. A. Steele, H. S. J. van der Zant, A. Castellanos-Gomez, Fast and broadband photoresponse of few-layer black phosphorus field-effect transistors, *Nano Lett.* 14 (6) (2014) 3347-3352.
- [39] Y. Chen, G. Jiang, S. Chen, Z. Guo, X. Yu, C. Zhao, H. Zhang, Q. Bao, S. Wen, D. Tang, D. Fan, Mechanically exfoliated black phosphorus as a new saturable absorber for both Q-switching and Mode-locking laser operation, *Opt. Express* 23 (2015) 12823-12833.
- [40] D. Li, H. Jussila, L. Karvonen, G. Ye, H. Lipsanen, X. Chen, Z. Sun, Polarization and thickness dependent absorption properties of black phosphorus: New saturable absorber for ultrafast pulse generation, *Sci. Rep.* 5 (2015) 15899.
- [41] J. Sotor, G. Sobon, M. Kowalczyk, W. Macherzynski, P. Paletko, K. M. Abramski, Ultrafast thulium-doped fibre laser mode locked with black phosphorus, *Opt. Lett.* 40 (16) (2015) 3885-3888.
- [42] Z. Qin, G. Xie, H. Zhang, C. Zhao, P. Yuan, S. Wen, L. Qian, Black phosphorus as saturable absorber for the -switched Er:ZBLAN fibre laser at 2.8 μm , *Opt. Express* 23 (2015) 24713-24718.
- [43] H. Mu, S. Lin, Z. Wang, S. Xiao, P. Li, Y. Chen, H. Zhang, H. Bao, S.P. Lau, C. Pan, D. Fan, Q. Bao, Black phosphorus-polymer composites for pulsed lasers, *Adv. Opt. Mater.* 3 (10) (2015) 14471453.
- [44] K. Park, J. Lee, Y. T. Lee, W. K. Choi, J. H. Lee, Y. W. Song, Black phosphorus saturable absorber for ultrafast modelocked pulse laser via evanescent field interaction, *Ann. Phys. (Berlin)* 527(11-12) (2015) 770-776.

[45] J. O. Island, G. A. Steele, H. S. J. van der Zant, A. C. Gomez, Environmental instability of few-layer black phosphorus, 2D Mater. 2 (1) (2015) 011002.

[46] A. Favron, E. Gaufrs, F. Fossard, A. L. P. L. Heures, N. Y. W. Tang, P.L. Lvesque, A. Loiseau, R. Leonelli, S. Francoeur, R. Martel, Photooxidation and quantum confinement effects in exfoliated black phosphorus, Nat. Mater. 14 (8) (2015) 826-832.

[47] J. Dai, X. C. Zeng, Structure and stability of two dimensional phosphorene with =O or =NH functionalization, RSC Adv. 4 (89) (2014) 48017-48021.

[48] X. Luo, Y. Rahbarihagh, J. Hwang, H. Liu, Y. Du, P. D. Ye, Temporal and thermal stability of Al₂O₃-passivated phosphorene mosfets, IEEE Electron Device Lett. 35 (12) (2014) 1314-1316.

[49] J. D. Wood, S. A. Wells, D. Jariwala, K. S. Chen, E. K. Cho, V. K. Sangwan, X. Liu, L. J. Lauhon, T. J. Marks, M. C. Hersam, Effective passivation of exfoliated black phosphorus transistors against ambient degradation, Nano Lett. 14 (12) (2014) 6964-6970.

[50] X. Chen, Y. Wu, Z. Wu, Y. Han, S. Xu, L. Wang, W. Ye, T. Han, Y. He, Y. Cai, N. Wang, High-quality sandwiched black phosphorus heterostructure and its quantum oscillations, Nat. Commun. 6 (2015) 7315

[51] R. A. Doganov, E. C. T. O'Farrell, S. P. Koenig, Y. Yeo, A. Ziletti, A. Carvalho, D. K. Campbell, D. F. Coker, K. Watanabe, T. Taniguchi, A. H. C. Neto, B. Ozyilmaz, Transport properties of pristine few-layer black phosphorus by van der Waals passivation in an inert atmosphere, Nat. Commun. 6 (2015) 6647.

[52] S. P. Koenig, R. A. Doganov, H. Schmidt, A. H. C. Neto, B. Ozyilmaz, Electric field effect in ultrathin black phosphorus, Appl. Phys. Lett. 104 (10) (2014) 103106.

[53] A. Castellanos-Gomez, L. Vicarelli, E. Prada, J. O. Island, K. L. Narasimha-Acharya, S. I. Blanter, D. J. Groenendijk, M. Buscema, G. A. Steele, J. V. Alvarez, H. W. Zandbergen, J. J. Palacios, H. S. J. van der Zant, Isolation and characterization of few-layer black phosphorus, 2D Mater. 1 (2) (2014) 025001.

[54] L. Song, L. Ci, H. Lu, P. B. Sorokin, C. Jin, J. Ni, A. G. Kvashnin, D. G. Kvashnin, J. Lou, B. I. Yakobson, P. M. Ajayan, Large scale growth and

characterization of atomic hexagonal boron nitride layers, *Nano Lett.* 10 (8) (2010) 3209-3215.

[55] F. Bonaccorso, A. Bartolotta, J. N. Coleman, C. Backes, 2D-crystal-based functional inks, *Adv. Mater.* Doi: adma2015006410 (2016).

[56] D. Hanlon, C. Backes, E. Doherty, C. S. Cucinotta, N. C. Berner, C. Boland, K. Lee, A. Harvey, P. Lynch, Z. Gholamvand, S. Zhang, K. Wang, G. Moynihan, A. Pokle, Q. M. Ramasse, N. McEvoy, W. J. Blau, J. Wang, G. Abellan, F. Hauke, A. Hirsch, S. Sanvito, D. D. O'Regan, G. S. Duesberg, V. Nicolosi, J. N. Coleman, Liquid exfoliation of solvent-stabilized few-layer black phosphorus for applications beyond electronics, *Nat. Commun.* 6 (2015) 8563.

[57] P. Yasaei, B. Kumar, T. Foroozan, C. Wang, M. Asadi, D. Tuschel, J.E. Indacochea, R. F. Klie, A. S. Khojin, High-quality black phosphorus atomic layers by liquid-phase exfoliation, *Adv. Mater.* 27 (11) (2015) 1887-1892.

[58] J. R. Brent, N. Savjani, E. A. Lewis, S. J. Haigh, D. J. Lewis, P. O'Brien, Production of few-layer phosphorene by liquid exfoliation of black phosphorus, *Chem. Commun.* 50 (2014) 13338.

[59] J. Kang, J. D. Wood, S. A. Wells, J. H. Lee, X. Liu, K. S. Chen, M. C. Hersam, Solvent exfoliation of electronic-grade, two-dimensional black phosphorus, *ACS Nano* 9 (4) (2015) 3596-3604.

[60] V. Scardaci, Z. Sun, F. Wang, A. G. Rozhin, T. Hasan, F. Hennrich, I. H. White, W. I. Milne, A. C. Ferrari, Carbon nanotube polycarbonate composites for ultrafast lasers, *Adv. Mater.* 20 (2008) 4040-4043.

[61] Y. Hernandez, V. Nicolosi, M. Lotya, F. M. Blighe, Z. Sun, S. De, I. T. McGovern, B. Holland, M. Byrne, Y. K. Gun'Ko, J. J. Boland, P. Niraj, G. Duesberg, S. Krishnamurthy, R. Goodhue, J. Hutchison, V. Scardaci, A. C. Ferrari, J. N. Coleman, High-yield production of graphene by liquid-phase exfoliation of graphite, *Nat. Nanotechnol.* 3 (9) (2008) 563-568.

[62] A. E. D. Rio-Castillo, C. Merino, E. D. Barra, E. Vázquez, Selective suspension of single layer graphene mechanochemically exfoliated from carbon nanofibres, *Nano Res.* 7 (7) (2014) 963-972.

- [63] Y. Mu and M. S. Si, The mechanical exfoliation mechanism of black phosphorus to phosphorene: A first-principles study, *Europhys. Lett.* 112 (3) (2015) 37003.
- [64] B. A. Pethicaa, L. Senaka, Z. Zhu, Anjing Lou, Surface and colloidal properties of cyclic amides. 5. N-cyclohexyl-2-pyrrolidone-water mixtures aggregation in solution and adsorption at the air-solution interface, *Colloids Surf., A* 186 (2001) 113-122.
- [65] A. Capasso, A. E. D. Rio-Castillo, H. Sun, A. Ansaldo, V. Pellegrini, F. Bonaccorso, Ink-jet printing of graphene for flexible electronics: An environmentally-friendly approach, *Solid State Commun.* 224 (2015) 53- 63.
- [66] J. Hassoun, F. Bonaccorso, M. Agostini, M. Angelucci, M. G. Betti, R. Cingolani, M. Gemmi, C. Mariani, S. Panero, V. Pellegrini, B. Scrosati, An advanced lithium-ion battery based on a graphene anode and a lithium iron phosphate cathode, *Nano Lett.* 14 (8) (2014) 4901-4906.
- [67] V. Sresht, A. A. H. Pádua, D. Blankschtein, Liquid-phase exfoliation of phosphorene: design rules from molecular dynamics simulations, *ACS Nano* 9 (8) (2015) 8255-8268.
- [68] Y. T. Liang, M. C. Hersam, Highly concentrated graphene solutions via polymer enhanced solvent exfoliation and iterative solvent exchange, *J. Am. Chem. Soc.* 132 (50) (2010) 17661-17663.
- [69] M. Sennett, E. Welsh, J.B. Wright, W.Z. Li, J.G. Wen, Z.F. Ren, Dispersion and alignment of carbon nanotubes in polycarbonate, *Appl. Phys. A* 76 (2003) 111-113.
- [70] T. D. Fornesa, J. W. Baur, Y. Sabbaa, E. L. Thomas, Morphology and properties of melt-spun polycarbonate fibres containing single- and multi-wall carbon nanotubes, *Polymer* 47 (2006) 1704-1714.
- [71] M. Zhang, E. J. R. Kelleher, T. H. Runcorn, V. M. Mashinsky, O. I. Medvedkov, E. M. Dianov, D. Popa, S. Milana, T. Hasan, Z. Sun, F. Bonaccorso, Z. Jiang, E. Flahaut, B. H. Chapman, A. C. Ferrari, S. V. Popov, and J. R. Taylor, Mid-

infrared raman-soliton continuum pumped by a nanotube-mode-locked sub-picosecond Tm-doped MOPFA, *Opt. Express* 21 (2013) 23261-23271.

[72] M. Parvin, J. G. Williams, The effect of temperature on the fracture of polycarbonate, *J. Mater. Sci.* 10 (11) (1975) 1883-1888.

[73] M. Chanda, S. K. Roy, *Plastics Technology Handbook*, Third edition, Technology & Engineering CRC Press 1998.

[74] A. O'Neill, U. Khan, P. N. Nirmalraj, J. Boland, J. N. Coleman, Graphene dispersion and exfoliation in low boiling point solvents, *J. Phys. Chem. C* 115 (2011) 5422-5428.

[75] Y. Wang, Z. Shi, J. Fang, H. Xu, J. Yin, Graphene oxide/polybenzimidazole composites fabricated by a solvent-exchange method, *Carbon* 49 (4) (2011) 1199-1207.

[76] H. Sun, A. E. D. Rio-Castillo, S. Monaco, A. Capasso, A. Ansaldo, M. Prato, D. A. Dinh, V. Pellegrini, B. Scrosati, L. Manna, F. Bonaccorso, Binder-free graphene as an advanced anode for lithium batteries, *J. Mater. Chem. A* 4, (2016), 6886-6895.

[77] L. Chen, G. Zhou, Z. Liu, X. Ma, J. Chen, Z. Zhang, X. Ma, F. Li, H. M. Cheng, W. Ren, Scalable clean exfoliation of high-quality few- layer black phosphorus for a flexible lithium ion battery, *Adv. Mater.* 28 (2016) 510517.

[78] W. Lu, H. Nan, J. Hong, Y. Chen, C. Zhu, Z. Liang, X. Ma, Z. Ni, C. Jin, Z. Zhang, Plasma-assisted fabrication of monolayer phosphorene and its Raman characterization, *Nano Res.* 7 (6) (2014) 853-859.

[79] Z. Guo, H. Zhang, S. Lu, Z. Wang, S. Tang, J. Shao, Z. Sun, H. Xie, H. Wang, X. F. Yu, P. K. Chu, From black phosphorus to phosphorene: Basic solvent exfoliation, evolution of Raman scattering, and applications to ultrafast photonics, *Adv. Funct. Mater.* 25 (2015) 6996-7002.

[80] R. Fei, L. Yang, Lattice vibrational modes and raman scattering spectra of strained phosphorene, *Appl. Phys. Lett.* 105 (8) (2014) 083120.

[81] Y. Cai, Q. Ke, G. Zhang, Y. P. Feng, V. B. Shenoy, Y. W. Zhang, Giant phononic anisotropy and unusual anharmonicity of phosphorene: Interlayer coupling and strain engineering, *Adv. Funct. Mater.* 25 (15) (2015) 2230-2236.

- [82] M. Elahi, K. Khaliji, S. M. Tabatabaei, M. Pourfath, R. Asgari, Modulation of electronic and mechanical properties of phosphorene through strain, *Phys. Rev. B* 91 (11) (2015) 115412.
- [83] A. Ziletti, A. Carvalho, P. E. Trevisanutto, D. K. Campbell, D. F. Coker, and A. H. Castro Neto, Phosphorene oxides: Bandgap engineering of phosphorene by oxidation, *Phys. Rev. B* 91 (2015) 085407.
- [84] J. Ribeiro-Soares, R. M. Almeida, L. G. Canado, M. S. Dresselhaus, A. Jorio, Group theory for structural analysis and lattice vibrations in phosphorene systems, *Phys. Rev. B* 91 (2015) 205421.
- [85] D. L. Allen, R. B. Allen, R. A. Wiercinski, High strength, reduced heat distortion temperature thermoplastic composition, *Google Patents* 4 (1988) 786.
- [86] M. Leigh, W. Shi, J. Zong, J. Wang, S. Jiang, N. Peyghambarian, Compact, single-frequency all-fibre Q-switched laser at 1 μm , *Opt. Lett.* 32 (8) (2007) 897-899.
- [87] L. Q. Zhang, Z. Zhuo, J. X. Wang, Y. Z. Wang, Passively Q-switched fibre laser based on graphene saturable absorber, *Laser Phys.* 22 (2) (2012) 433-436.
- [88] K. Wu, X. Zhang, J. Wang, X. Li, J. Chen, WS_2 as a saturable absorber for ultrafast photonic applications of mode-locked and Q-switched lasers, *Opt. Express* 23 (9) (2015) 11453-11461.

Figure 1: (a) Absorption spectra of FL-BP dispersion in CHP (orange curve) and chloroform (CHCl_3 , blue curve). (b) Raman spectra of the bulk BP (black curve), the exfoliated FL-BP in CHP (orange curve) and the exchanged FL-BP in chloroform (blue curve). (c) Schematic representation of BP and the actively vibrational modes of Raman spectroscopy. TEM images of exfoliated FL-BP in (d) CHP and (e) chloroform, respectively and (f) their respective histogram of lateral sizes.

Figure 2: Raman spectra of FL-BP in chloroform (blue curve), the bare polycarbonate pellets (grey curve) and the blending FL-BP/PC (brown curve).

Figure 3: Stability comparison between mechanically exfoliated BP flakes and PC/FL-BP composite in ambient atmosphere. (a) Transmittance as a function of time. Input power: 10 mW. Morphologies of mechanically exfoliated BP on the surface of fibre connector before (b) and after (c) measurement for 336 hours. Morphologies of PC/FL-BP composite on the surface of fibre connector before (d) and after (e) measurement for 336 hours. Green dashed and red solid circles denote the profiles of fibre cladding and core, respectively.

Figure 4: The schematic of the Q-switched fibre laser. LD, laser diode; WDM, wavelength division multiplexer; EDF, Erbium doped fibre; ISO, polarization independent isolator. Inset: the PC/FL-BP composite SA fibre device.

Figure 5: Q-switched laser performances. (a) Output pulse train. (b) Single pulse envelope. Inset: output spectrum. (c). Output pulse repetition rate and pulse duration as a function of the pump power, respectively. (d) Output power and pulse energy as a function of the pump power, respectively.

Black phosphorus polycarbonate polymer composite for pulsed fibre lasers

Diao Li^{a,b}, Antonio Esau Del Rio Castillo^c, Henri Jussila^a, Guojun Ye^{d,e}, Zhaoyu Ren^b, Jintao Bai^b, Xianhui Chen^{d,e,f}, Harri Lipsanen^a, Zhipei Sun^a, Francesco Bonaccorso^{c,2}

^aDepartment of Micro- and Nanosciences, Aalto University, P.O. Box 13500, FI-00076 Aalto, Finland

^bInstitute of Photonics and Photo-technology, Northwest University, Xi'an, 710069, China

^cIstituto Italiano di Tecnologia, Graphene Labs 16163, Genova, Italy

^dHefei National Laboratory for Physical Science at Microscale and Department of Physics, University of Science and Technology of China, Hefei, 230026, China

^eKey Laboratory of Strongly-coupled Quantum Matter Physics, University of Science and Technology of China, Chinese Academy of Sciences, Hefei, 230026, China

^fCollaborative Innovation Center of Advanced Microstructures, Nanjing, 210093, China

Graphical abstract

² Email address: francesco.bonaccorso@iit.it; zhipei.sun@aalto.fi