Research article

Bingzheng Yan, Guoru Li, Bingnan Shi, Juntong Liu, Hongkun Nie, Kejian Yang, Baitao Zhang* and Jingliang He

2D tellurene/black phosphorus heterojunctions based broadband nonlinear saturable absorber

<https://doi.org/10.1515/nanoph-2020-0174>

Received March 6, 2020; accepted April 2, 2020

Abstract: Two-dimensional (2D) mono-elemental materials (Xenes) show remarkable potential in the fields of fundamental science and technology, have been regarded as a wide range of building blocks for electronic technologies due to their unique chemical, physical, electrical, and optical properties. Here, 2D tellurene/black phosphorus (Te/BP) heterojunctions are successfully fabricated through liquid-phase exfoliation (LPE) method. Their nonlinear optical absorption properties at 1.0, 2.0, and 2.8 μm have been studied by an open-aperture Z-scan method. The results revealed the excellent broadband saturable absorption responses of the prepared BP/Te heterojunctions, which are further confirmed by using them as saturable absorbers (SAs) for passively Q-switched all-solid-state lasers operating at 1.0, 2.0, and 2.8 μm , respectively. In particular, 1.04 μm continuous-wave (CW) mode-locked lasers with a pulse width of 404 fs is realized for the first time, to our best knowledge. Our work indicates that 2D Xenes especially 2D Xenes based heterojunctions have great potential in the fields of pulsed laser generation/modulation and other optoelectronic and photonic devices.

Keywords: black phosphorus; heterojunction; saturable absorber; tellurene; xenes.

1 Introduction

In the past decades, encouraged by the significant success of graphene [1–3], two-dimensional (2D) materials have evoked tremendous interest because of their exotic properties (electronic, photonic, magnetic, and catalytic, etc.) caused by the ultrathin 2D structure. To date, a number of 2D materials have been developed and widely applied in the fields including (opto)electronics, photonics, environment science, energy, biomedicines, and so on [4–9]. Classified by the composition, 2D materials can be divided into two categories: one is multi-elemental materials (chemical compounds), such as hexagonal boron nitride (h-BN), transitional metal dichalcogenides (TMDs) [10, 11], nitrides and carbonitrides (Mxenes) [12, 13], etc.; the other is mono-elemental 2D materials (Xenes, “X” represents single elements) [14–18], such as group-III (borophene [19], gallenene), –IV (graphene [1, 2], silicene [14, 20], germanene [20], and stanene [20]), –V (black phosphorus (BP) [21, 22], arsenene [18], and antimonene [18, 23]), and VI (tellurene [24, 25]) elemental materials. Compared with other 2D materials, 2D Xenes have the tunable layer-dependent bandgaps, leading to the potential of bridging the bandgap space between graphene (zero bandgap), Mxenes (limited bandgaps), TMDs (large bandgaps), and h-BN (insulator). In this case, it can be easily to manipulate the interaction between electro-magnetic waves and Xenes in the wavelength region from ultraviolet to near-infrared (NIR) and even mid-infrared (MIR) [17]. In addition, 2D Xenes not only have the same electronic properties as graphene (e. g., linear dispersion electronic band structure and high Fermi velocity), but also possess an open bandgap at the Dirac point and strong spin-orbit coupling [26]. Moreover, their electronic properties and quantum phenomena can be induced and easily tuned by manipulating the Xene-substrate interaction and Xene-interlayer twisting [18]. Therefore, 2D Xenes have the potential to break through the limitations of other 2D materials in practical applications.

Group V BP, thoroughly studied as a 2D layered material since early 2014 [27], is now the most extensively

***Corresponding author: Baitao Zhang**, State Key Laboratory of Crystal Materials, Shandong University, Jinan, 250100, PR China; and Key Laboratory of Laser & Infrared System, Ministry of Education, Shandong University, Qingdao, 266237, PR China, E-mail: btzhang@sdu.edu.cn. <https://orcid.org/0000-0001-9105-0684>

Bingzheng Yan, Guoru Li, Bingnan Shi, Juntong Liu and Hongkun Nie: State Key Laboratory of Crystal Materials, Shandong University, Jinan, 250100, PR China. <https://orcid.org/0000-0002-3937-0389> (B. Yan)

Kejian Yang and Jingliang He: State Key Laboratory of Crystal Materials, Shandong University, Jinan, 250100, PR China; Key Laboratory of Laser & Infrared System, Ministry of Education, Shandong University, Qingdao, 266237, PR China

studied 2D Xene after graphene due to the fascinating properties, such as layer-dependent direct bandgap (~ 0.3 – 2.0 eV), in-plane anisotropy, large room-temperature hole mobility ($>10^3$ cm²/V/s), and self-biodegradation [28]. These outstanding properties makes BP to be promising for scientific research and development of electronic, optoelectronic and bio-medicine devices. Group VI tellurene (Te) is a narrow-bandgap p-type semiconductor with unique one-dimensional (1D) van der Waals crystal structure. Te atoms are covalently bonded into skew-symmetric helical chains, while the neighboring chains are bonded by van der Waals forces in other two dimensions to form a trigonal crystal structure [29]. Te also has layer-dependent direct bandgap: ~ 0.33 eV for the bulk and ~ 0.92 eV for monolayer [30], indicating the response band from visible to MIR region [31]. Up to now, Te has been successfully applied in FETs, photodetectors and nonlinear photonic devices [26, 31–34] due to the advantages of high carrier mobility [35], high piezoelectricity [36], low lattice thermal conductivity [37], and excellent air-stable performance at room temperature [34]. Recently, it has been reported that by combining Te and BP, e. g., BP doped with Te, the optoelectronic performance would be greatly improved [38–40].

Besides doping, another effective way to combine 2D Te and BP together is to form Te/BP heterojunctions [41–44] without considering the atomic commensurability as in their bulk counterparts benefiting from the weak van der Waals forces of 2D layered materials. Here, we synthesize the 2D Te/BP heterojunction nanosheets through the commonly used liquid-phase exfoliation (LPE) method. The nonlinear optical absorption properties at 1.0, 2.0, and 2.8 μm are investigated by the open-aperture Z-scan method, revealing the excellent broadband saturable absorption responses of 2D Te/BP heterojunction nanosheets. With the prepared 2D Te/BP heterojunction nanosheets as SA, the efficient passively Q-switched (PQS) solid-state lasers operating at 1.0, 2.0, and 2.8 μm are demonstrated. The PQS laser performances are much better than that of using 2D Te nanosheets as SA. Furthermore, 1.04 μm passively mode-locked lasers with a pulse width of 404 fs is realized. Our work paves a new way of 2D Xenex especially 2D Xenex based heterojunctions in the applications of pulsed laser generation/modulation and other optoelectronic devices.

2 Preparation and characterization

LPE is a convenient, practical and commonly used method for fabricating 2D layered materials [45, 46]. Strong

anisotropy of BP and Te existing between intra- and inter-chains or layers provides the opportunities to fabricate the 2D layered nanosheets from their bulk counterparts through LPE method. The fabrication process is as following: first, mono-crystal Te and BP with a purity of 99.9999% was ground into powders respectively, and then mixed together. Second, the mixed powders were ultrasonicated in isopropyl alcohol (IPA) for a few hours. In this contribution, subjected to sonication in IPA, 3D bulk particles were gradually exfoliated into 2D layered nanosheets and connected by van der Waals force to form the heterojunction nanostructure. Third, the as-prepared solutions were centrifuged at 5000 rpm for 10 min. Finally, the supernatant liquors were uniformly transferred onto a sapphire substrate by spin coating method and dried in a vacuum oven at room temperature for 24 h to prevent oxidation. For comparison, single element 2D Te nanosheets were prepared under the same condition.

The surface morphologies of the prepared 2D Te/BP heterojunction nanosheets were examined by transmission electron microscopy (TEM) and atomic force microscopy (AFM) measurements. Figure 1a shows the typical TEM image with the size ranging from 100 to 200 nm, in which the dark part illustrates the well integration of the two materials. The high-resolution transmission electron microscopy (HRTEM) image shown in Figure 1b clearly exhibits the lattice structures of Te and BP and the corresponding border line, which further confirms the 2D Te/BP heterojunction nanostructure. Figure 1c shows the TEM mapping image also gives a convincing evidence that the Te and BP combine (the ratio of the connection is $>85\%$) successfully. Figure 1d presents the energy-dispersive X-ray spectroscopy (EDS) image of the exfoliated 2D Te/BP heterojunction nanosheets. The atomic ratio of Te and P is approximately 1:1, indicating the purity of the sample. The AFM image in Figure 1e indicates that the 2D Te/BP nanosheets are uniformly distributed on the substrate. The average thickness is determined to be about 15 nm (see Figure 1f).

The X-ray diffraction (XRD) pattern of the prepared 2D Te/BP nanosheets in Figure 2a shows the typical diffraction peaks of Te and BP (red for BP and blue for Te), which is consistent with the previous works [33, 40], indicating that crystal structure remain unchanged during the exfoliation process. Figure 2b presents the corresponding Raman spectra excited by a 532 nm laser source. Typical Raman peaks located at 104.2 cm⁻¹ (E_1), 120.4 cm⁻¹ (A_1), 140.3 cm⁻¹ (E_2) for Te (blue) and 360.8 cm⁻¹ (A_g^1), 434.9 cm⁻¹ (B_{2g}), 462.1 cm⁻¹ (A_g^2) for BP (red) are obviously observed, which are also consistent with previous works [25, 27]. X-ray

Figure 1: (a–c) TEM, HRTEM and TEM mapping images of the 2D Te/BP nanosheets. (d) EDS image and the corresponding atomic ratio of the 2D Te/BP nanosheets. (e, f) The AFM image and thickness distribution of the 2D Te/BP nanosheets.

Figure 2: (a) The X-ray diffraction (XRD) patterns of the prepared Te/BP heterojunction nanosheets, the blue (color) represents the diffraction peaks of Te, and the red is for BP. (b) Raman spectra of the Te/BP heterojunction nanosheets. (c, d) XPS image of the elements P and Te in the Te/BP heterojunction nanosheets. (e) UV-VIS-NIR spectra of the prepared 2D Te/BP heterojunction nanosheets, inset: Tauc plot of $(\alpha h\nu)^2$ versus $h\nu$.

Figure 3: Open-aperture Z-scan curves of the 2D Te/BP heterojunction nanosheets based SA at the three wavelengths of (a) 1.0, (b) 2.0, and (c) 2.8 μm , respectively.

photoelectron spectroscopy (XPS) is measured and shown in Figure 2c, d. The P $2p_{3/2}$ and $2p_{1/2}$ peaks located at 133.9 and 134.9 eV, and the Te $3d_{5/2}$ and $3d_{3/2}$ peaks located at 572.9 and 583.2 eV are observed. The UV-VIS-NIR transmission spectra is shown in Figure 2e (the background of the substrate and Fresnel reflection has been subtracted), indicating the broadband optical absorption of the 2D Te/BP heterojunction nanosheets. By using the Tauc method [47], the optical bandgap of the prepared 2D Te/BP heterojunction nanosheets is determined to be 0.4 ± 0.02 eV. The narrow band gap further confirms that the optical response of 2D Te/BP heterojunction nanosheets can be extended to the mid-infrared (MIR) region.

3 Broadband nonlinear optical absorption response

According to report, heterojunction structure leads to electron transfer process, increased light absorption and reduced relaxation time, which is benefit to enhance the optical nonlinearity [48, 49]. The broadband nonlinear saturable absorption properties of the prepared 2D Te/BP heterojunction nanosheets are investigated by the open aperture Z-scan method (see Figure S1). The details are described in the experimental section. The three Z-scan curves shown in Figure 3a–c exhibit sharp and narrow peaks at the focus position, indicating the typical saturable absorption

behavior of the prepared 2D Te/BP heterojunction nanosheets at 1.0, 2.0, and 2.8 μm , respectively. As well known that the saturable absorption response of the 2D materials is mainly caused by the Pauli blocking effect and can be used as saturable absorber (SA), which is a key element for passively Q-switched (PQS) and mod-locked lasers.

To get the saturable absorber parameters of the prepared 2D Te/BP heterojunction nanosheets based SA, the Z-scan curves can be fitted by the following formulas [50]:

$$T_n = \left(1 - \frac{\Delta R \times I_s}{I_s + \frac{I_0}{1 + \frac{Z^2}{Z_0^2}}} \right) / (1 - \Delta R) \quad (1)$$

where T_n is the nonlinear transmittance, I_0 and I_s are the incident and saturable intensity, ΔR is the modulation depth, Z and Z_0 are relative position of the sample to the focus position and the Rayleigh length of the input beam. By fitting the Z-scan curves in Figure 3, the unsaturable loss, saturation fluence, and modulation depth of the 2D Te/BP heterojunction nanosheets based SA at 1.0, 2.0, and 2.8 μm are determined and summarized in Table 1. The results indicate that it has great potential for application as the broadband optical Q-switch for PQS and mode-locked lasers. The nonlinear transmission curves as a function of the incident energy intensity are also measured by the balanced dual-detector method (see Figure S2), which

further illustrate the saturable absorption properties of the prepared 2D Te/BP heterojunction nanosheets at the three wavelengths.

4 Broadband passively Q-switched solid-state lasers with 2D Te/BP heterojunction nanosheets based SA

To further investigate the broadband saturable absorption properties of the prepared 2D Te/BP heterojunction nanosheets, it was inserted into a compact two-mirror laser cavity with three different laser crystals to generate PQS laser pulses. The laser experimental setup is shown in Figure S3 and the details are described in the experimental

section. To obtain efficient PQS lasers, the so-called second threshold condition must be satisfied, which can be simplified for 2D materials-based SA and described as [51]:

$$\frac{F_{\text{sat},A}}{\Delta R\tau} \leq \frac{2hc\omega_{\text{eff},L}^2}{m\lambda\sigma_{\text{em},L}\omega_{\text{eff},A}^2 T_R} \quad (2)$$

where $F_{\text{sat},A}$ is the saturable energy fluence, τ is the recovery time of the SA (here we assume it is in the same scale of BP), h is the Planck constant, c is the light velocity, λ is the laser wavelength, $\omega_{\text{eff},A}$ and $\omega_{\text{eff},L}$ are the effective laser radii at the position of SA and laser crystal, $\sigma_{\text{em},L}$ is the stimulated emission cross-section of the laser crystal, T_R is the laser cavity round-trip time, and m is a cavity constant ($m = 1, 2$ for ring and linear cavity). Considering the characters of three laser crystals, the cavity parameters, and the SA parameters, the value of the left side of Equation (2) is calculated to be much smaller than that of the right side (Table S1), which further confirms that the prepared 2D Te/BP heterojunction nanosheets based SA is suitable for generating PQS laser pulse with the designed laser cavity.

The average output power versus absorbed pump power of continuous-wave (CW) and PQS laser operations at the three wavelengths are shown in Figure S4a–c. The average output power increases as the increase of the pump power.

Table 1: Saturable absorption parameters of 2D Te/BP heterojunction nanosheets based SA.

Parameters	1.0 μm	2.0 μm	2.8 μm
Unsaturable loss (%)	9.83	7.61	7.28
Modulation depth (%)	13.6	12.6	10.3
Saturation intensity (kW/cm^2)	540	690	260

Figure 4: The typical pulse profile of the shortest pulse width and the corresponding pulse train at the maximum output power at the three wavelengths of (a) 1.0, (b) 2.0, and (c) 2.8 μm , respectively.

Table 2: 2D BP, Te, and Te/BP heterojunction nanosheets SA based passively Q-switched lasers at 1.0, 2.0, and 2.8 μm .

	1.0 μm			2.0 μm			2.8 μm		
	BP	Te	Te/Bp	BP	Te	Te/Bp	BP	Te	Te/Bp
Wavelength (nm)	1064	1064.3	1064.4	1988	1954.4	1956.6	2950	2790.0	2792.0
Output power (W)	0.126	0.305	0.312	0.151	1.037	1.006	0.385	0.34	0.33
Pulse width (ns)	144	437	329	1780	451	250	194.3	256	163
Repetition rate (kHz)	692.5	71	126	19.25	65	83	158.7	90	151
Single pulse energy (μJ)	0.18	4.30	2.48	7.84	15.95	12.12	2.43	3.89	1.92
Peak power (W)	1.26	9.83	7.53	23.8	35.37	48.48	12.5	12.79	11.78
Reference	[52]	This work		[53]	This work		[54]	This work	

No damage of the laser crystal and SA are observed in the range of the pump power used in our experiment. Figure S4d–f present the output spectra of the CW and PQS laser at the maximum average output power. An obvious spectral blueshift and line width compression are observed from the PQS spectra. It may be caused by the insertion loss induced by the SA. The pulse width and repetition rate versus the absorbed pump power are shown in Figure S5a–c. The pulse width decreases, and the repetition rate increases as the pump power increases. The shortest pulse widths for the three wavelengths were determined to be 329, 250 and 163 ns for 1.0, 2.0, and 2.8 μm , corresponding to the largest repetition rate of 126, 83, and 151 kHz, respectively. The typical pulse profile of the shortest pulse width and the corresponding pulse train at the maximum output power are shown in Figure 4. The pulse-to-pulse amplitude instability were recorded and calculated to be less than 3.8% in one-hour operation for the three PQS lasers. Clean and tidy pulse trains demonstrate the excellent saturable absorption properties of 2D Te/BP heterojunction nanosheets based SA. The PQS results at the three wavelengths with the 2D Te/BP heterojunction nanosheets based SA and single 2D BP and Te (Fabricated under the same condition, $\Delta R = 9.6, 8.4$, and 7.2% , and $I_s = 680, 910$, and 430 kW/cm^2 for 1.0, 2.0, and 2.8 μm) are summarized in Table 2. The results are comparable to that of single 2D BP and Te nanosheets, shows great potential in short pulses and high peak power, as well as other 2D materials, such as graphene, MoS_2 . Furthermore, compared with BP, after one-month store in air at room temperature, the sample could also be used, which indicates the high stability of 2D Te/BP heterojunction nanosheets.

5 Continuous-wave mode-locked solid-state lasers operating at 1.0 μm

Besides PQS, another important application of SA is utilized as a key optical modulator to realize the mode-locking

operation, which is the main technique of generating ultrafast pulsed lasers. However, to realize 2D material-SA based continuous-wave (CW) mode-locking is much more difficult than that of PQS, especially for solid-state bulk lasers. To obtain the stable CW mode-locked solid-state laser operation, the following classical equation must be satisfied [51]:

$$F_{\text{sat},A} \Delta R < \frac{(PT_R)^2}{F_{\text{sat},L} A_{\text{eff},L} A_{\text{eff},A}} = \frac{(PT_R)^2 \times m \sigma_{\text{em},L} \lambda}{hc \times \pi \omega_{\text{eff},L}^2 \times \pi \omega_{\text{eff},A}^2} \quad (3)$$

which means that the mode-locking pulse energy must be larger than the minimum intracavity pulse energy, i. e., the saturation fluence of SA. In Equation (3), P is laser power in the laser cavity, T_R is the round-trip time, $A_{\text{eff},A}$ and $A_{\text{eff},L}$ are the laser mode areas on SA and laser crystal. Here, as shown in Figure S6, a 3.55 m long z-type resonator is designed with Yb:KYW as the gain medium. The experimental details are described in the experimental section. Considering the laser crystal properties, A parameters and cavity design, the left-hand side of Equation (3) is calculated to be $2.2 \mu\text{J/cm}^2$, much smaller than that of the right-hand side ($52.5 \mu\text{J/cm}^2$). Therefore, stable CW mode-locked lasers can be obtained with the as-prepared 2D Te/BP heterojunction nanosheets SA and the as-designed laser cavity.

Insert the prepared 2D Te/BP heterojunction nanosheets based SA into the laser resonator, increase the pump power and carefully adjust the resonator, the laser firstly operates at the unstable Q-switched mode-locking regime, and finally turns into the stable CW mode-locked laser operation. Under the absorbed pump power of 6.17 W, a maximum average output power of 292 mW is obtained. Further increase the pump power, CW mode-locking become unstable. The output power instabilities (RMS) were measured to be less than 3% over 3 h. Figure 5a shows the output laser pulse trains in the time scale of 0.5 and 5 ms at the maximum output power, illustrating the stable

Figure 5: Recorded results of Te/BP heterojunction SAM-based mode-locked laser. (a) Recorded CWML pulse trains under the maximum pump power. (b, c) Measured Autocorrelation trace for 404 fs and the corresponding spectrum. (d, e) Recorded frequency spectrum with a wide and a narrow span respectively.

Table 3: Comparison of 2D BP, Te, and Te/BP heterojunction nanosheets SA based mode-locked lasers.

Materials	Gain-medium	Wavelength(nm)	Output power (mW)	Single-pulse energy (nJ)	Pulse width (ps)	Ref.
Te/BP	Yb KYW	1049.1	292	6.94	404	This work
Te	Yb KYW	1048.4	269	6.41	468	
Te	Er fiber	1556.6	5.3	0.34	0.83	[55]
Te	Er fiber	1574.0	23.61	1.94	5.87	[56]
BP	Yb fiber	1085.6	80	5.93	7.54	[57]
BP	Yb fiber	1030.6	32.5	0.70	400	[58]
BP	Nd YVO4	1064.1	460	3.29	6.10	[59]
BP	Yb Lu: CALGO	1053.4	820	6.48	0.272	[60]

CW mode-locking operation. Figure 5b, c present the mode-locked laser spectrum with an FWHM of 3.28 nm and the pulse duration, which is measured to be 404 fs by sech² pulse shape fitting. The corresponding time bandwidth product is ~0.364, lightly larger than the Fourier transform-limited value (0.315), indicating that the output pulses are slightly chirped. What's more, the radio-frequency (RF) spectra at different spans are recorded by a spectrum analyzer (Agilent N9000A). As shown in Figure 5d, a clear and sharp peak located at 42.1 MHz with the signal-to-noise ratio of 61 dB is observed. No spurious modulation signal exists in the RF spectra, proving clean CW mode-locking pulses based 2D Te/BP heterojunction nanosheets have been achieved. To evaluate the stability of the CW mode-locking laser, a wide span of 1000 MHz with RBW of 110 kHz was recorded in Figure 5e. For comparison, 2D Te nanosheets SA based mode-locked laser is also achieved under the same condition. The experimental results are

shown in Figure S7. A pulse width of 468 fs with time bandwidth product of 0.373 is obtained. The comparisons of 2D BP, Te and Te/BP heterojunction nanosheets SA based mode-locked lasers are shown in Table 3. As you can see from the table, the Te/BP heterojunction SA based mode-locked laser is superior to most of others in high single-pulse energies and short pulse width, indicate that 2D Te/BP heterojunction nanosheets has the potential to be a new generation SA material for ultrafast laser generations.

6 Conclusion

In summary, we fabricated the 2D Te/BP heterojunction nanosheets by LPE method. Using open aperture Z-scan methods, the broadband nonlinear optical absorption properties are investigated. The results indicating the

excellent saturable absorption response of the 2D Te/BP heterojunction nanosheets, which is further confirmed by using as the SA for broadband PQS lasers operating at 1.0, 2.0, and 2.8 μm , respectively. Furthermore, CW mode-locked solid-state laser with the pulse as short as 404 fs and maximum output power of 292 mW is demonstrated for the first time, indicating the potential of 2D Te/BP heterojunction nanosheets for ultrafast photonics application. Our work delivers a fresh insight into tailoring 2D Xenex and related heterojunctions so as to develop desired photonic materials, which may find wide applications for pulse laser generation and all-optical signal processing.

7 Experimental section

Open-aperture Z-scan measurements: Open-aperture Z-scan measurements were performed using a homemade picosecond laser: 30 ps, 40 MHz for 1.0, 2.0, and 2.8 μm respectively. The experimental setup is shown in Figure S1, in which two-beam balanced Z-scan measurements is used, i. e., the excited laser beam was split into two parts: one part is measured by a power meter (Thorlabs S470C) and applied as the reference beam, and the other is focused by a lens (100 mm) with beam radius of $\sim 110 \mu\text{m}$ and passes through the samples. The sample is fixed on a stepper auto-motor.

Passively Q-switched lasers: The experimental setup is shown in Figure S3. Three different crystals Nd:YAG, Tm:YAP, and Er:YSGG are used for generating lasers operating at 1.0, 2.0, and 2.8 μm . The length of the laser cavity is $\sim 20 \text{ mm}$. The input mirrors (IMs) with a curvature radius of 200 mm are antireflection-coated at the corresponding pump wavelength (808 nm for Nd:YAG, 792 nm for Tm:YAP, and 967 nm for Er:YSGG) and high-reflection-coated at the corresponding output wavelength (1064 nm for Nd:YAG, 1980 nm for Tm:YAP, and 2800 nm for Er:YSGG), while the output mirrors (OMs) are flat mirrors with a partial-transmissivity of 4% for the corresponding output wavelength, respectively. To remove the excess thermal effect, all the gain mediums were wrapped by indium foil and mounted in a copper block with water cooled at 16°C.

CW mode-locking lasers: The experimental setup is shown in Figure S4. Yb:KYW is used as the gain medium. The as-prepared 2D Te/BP heterojunction nanosheets are directly spin-coated on a high-reflection mirror coating at 1020–1100 nm as the saturable absorber mirror (SAM), and places on the five-dimensional mobile platform to precisely control the oscillating spot size. IM is a flat mirror with the

high-reflection-coated at 1000–1100 nm and antireflection-coated at 976 nm. M1 and M2 are also high-reflection-coated at the wavelength of 1000–1100 nm with the curvature radius of 800 and 200 mm, respectively. The OC is a plane mirror with transmittance of 1% at 1040 nm. To compensate for the normal group delay dispersion (GDD) in the mode-locking cavity, a Gires–Tournois interferometer (GTI) mirror with a total of -500 fs^2 GDD per round is used.

Acknowledgements: The authors thank Prof. Han Zhang from Shenzhen University for the kind suggestions about the materials fabrication and characterization. This work was supported by the National Natural Science Foundation of China (NSFC) (Grant No. 61675116, 61575110), the Major Research and Development Program for Public Welfare in Shandong (2017GGX20134), the Young Scholars Program of Shandong University (Grant No. 2017WLJH48), Key research and development program of Shandong Province (2018GGX101006), Shenzhen Science and Technology Research and Development Funds (JCYJ 20180305163932273).

Reference

- [1] K. S. Novoselov, A. K. Geim, S. V. Morozov, et al., “Electric field effect in atomically thin carbon films,” *Scienc*, vol. 5696, pp. 666–669, 2004, <https://doi.org/10.1126/science.1102896>.
- [2] A. K. Geim and K. S. Novoselov, “The rise of graphene,” *Nat. Mater.*, vol. 3, pp. 183–191, 2007, <https://doi.org/10.1038/nmat1849>.
- [3] Q. Bao, H. Zhang, Y. Wang, et al., “Atomic-layer graphene as a saturable absorber for ultrafast pulsed lasers,” *Adv. Funct. Mater.*, vol. 19, pp. 3077–3083, 2009.
- [4] A. Gupta, T. Sakthivel, and S. Seal, “Recent development in 2D materials beyond graphene,” *Progress Mater. Sci.*, vol. 73, pp. 44–126, 2015, <https://doi.org/10.1016/j.pmatsci.2015.02.002>.
- [5] F. Xia, H. Wang, D. Xiao, M. Dubey, and A. Ramasubramaniam, “Two-dimensional material nanophotonics,” *Nat. Photon.*, vol. 12, pp. 899, 2014, <https://doi.org/10.1038/nphoton.2014.271>.
- [6] Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, and M. S. Strano, “Electronics and optoelectronics of two-dimensional transition metal dichalcogenides,” *Nat. Nanotechnol.*, vol. 11, pp. 699, 2012.
- [7] T. Low, A. Chaves, J. D. Caldwell, et al., “Polaritons in layered two-dimensional materials,” *Nat. Mater.*, vol. 2, pp. 182–194, 2017.
- [8] Z. Sun, A. Martinez, and F. Wang, “Optical modulators with 2D layered materials,” *Nat. Photon.*, vol. 4, pp. 227–238, 2016, <https://doi.org/10.1038/nphoton.2016.15>.
- [9] S. Das, M. Kim, J.-W. Lee, and W. Choi, “Synthesis, properties, and applications of 2-D materials: a comprehensive review,” *Crit. Rev.*

- Solid State Mater. Sci.*, vol. 39, pp. 231–252, 2014, <https://doi.org/10.1080/10408436.2013.836075>.
- [10] S. Manzeli, D. Ovchinnikov, D. Pasquier, O. V. Yazyev, and A. Kis, “2D transition metal dichalcogenides,” *Nat. Rev. Mater.*, vol. 8, pp. 17033, 2017, <https://doi.org/10.1038/natrevmats.2017.33>.
 - [11] K. F. Mak, C. Lee, J. Hone, J. Shan, and T. F. Heinz, “Atomically thin: a new direct-gap semiconductor,” *Phys. Rev. Lett.*, vol. 105, pp. 136805, 2010, <https://doi.org/10.1103/PhysRevLett.105.136805>.
 - [12] J.-C. Lei, X. Zhang, and Z. Zhou, “Recent advances in MXene: preparation, properties, and applications,” *Front. Phys.*, vol. 10, pp. 276–286, 2015, <https://doi.org/10.1007/s11467-015-0493-x>.
 - [13] X. Jiang, S. Liu, W. Liang, et al., “Broadband nonlinear photonics in few-layer MXene $\text{Ti}_3\text{C}_2\text{Tx}$ ($\text{T} = \text{F}, \text{O}, \text{or OH}$),” *Laser Photon. Rev.*, vol. 12, pp. 1700229, 2018, <https://doi.org/10.1002/lpor.201870013>.
 - [14] N. J. Roome, and J. D. Carey, “Beyond graphene: stable elemental monolayers of silicene and germanene,” *ACS Appl. Mater. Interfaces*, vol. 6, pp. 7743–7750, 2014, <https://doi.org/10.1021/am501022x>.
 - [15] X. Kong, Q. Liu, C. Zhang, Z. Peng, and Q. Chen, “Elemental two-dimensional nanosheets beyond graphene,” *Chem. Soc. Rev.*, vol. 46, pp. 2127–2157, 2017, <https://doi.org/10.1039/c6cs00937a>.
 - [16] A. J. Mannix, B. Kiraly, M. C. Hersam, and N. P. Guisinger, “Synthesis and chemistry of elemental 2D materials,” *Nat. Rev. Chem.*, vol. 2, pp. 0014, 2017, <https://doi.org/10.1038/s41570-016-0014>.
 - [17] A. Molle, J. Goldberger, M. Houssa, Y. Xu, S. C. Zhang, and D. Akinwande, “Buckled two-dimensional Xene sheets,” *Nat. Mater.*, vol. 16, pp. 163–169, 2017, <https://doi.org/10.1038/nmat4802>.
 - [18] M. Pumera and Z. Sofer, “2D monoelemental arsenene, antimonene, and bismuthene: beyond bPhosphorus,” *Adv. Mater.*, vol. 21, pp. 1605299, 2017.
 - [19] A. J. Mannix, Z. Zhang, N. P. Guisinger, B. I. Yakobson, and M. C. Hersam, “Borophene as a prototype for synthetic 2D materials development,” *Nat. Nanotechnol.*, vol. 13, pp. 444–450, 2018, <https://doi.org/10.1038/s41565-018-0157-4>.
 - [20] S. Balendhran, S. Walia, H. Nili, S. Sriram, and M. Bhaskaran, “Elemental analogues of graphene: silicene, germanene, stanene, and phosphorene,” *Small*, vol. 11, pp. 640–652, 2015, <https://doi.org/10.1002/sml.201402041>.
 - [21] K. Cho, J. Yang, and Y. Lu, “Phosphorene: an emerging 2D material,” *J. Mater. Res.*, vol. 15, pp. 2839–2847, 2017.
 - [22] S. C. Dhanabalan, J. S. Ponraj, Z. Guo, S. Li, Q. Bao, and H. Zhang, “Emerging trends in phosphorene fabrication towards next generation devices,” *Adv. Sci. (Weinh)*, vol. 4, pp. 1600305, 2017, <https://doi.org/10.1002/advs.201600305>.
 - [23] L. Lu, X. Tang, R. Cao, et al., “Broadband nonlinear optical response in few-layer antimonene and antimonene quantum dots: a promising optical Kerr media with enhanced stability,” *Adv. Opt. Mater.*, vol. 44, pp. 1700301, 2017, <https://doi.org/10.32604/jaop.2018.04232>.
 - [24] L. Xian, A. Pérez Paz, E. Bianco, P. M. Ajayan, and A. Rubio, “Square selenene and tellurene: novel group VI elemental 2D materials with nontrivial topological properties,” *2D Mater.*, vol. 4, pp. 041003, 2017, <https://doi.org/10.1088/2053-1583/aa8418>.
 - [25] Q. Wang, M. Safdar, K. Xu, M. Mirza, Z. Wang, and J. He, “Van der Waals epitaxy and photoresponse of hexagonal tellurium nanoplates on flexible mica sheets,” *ACS Nano*, vol. 7, pp. 7497–7505, 2014.
 - [26] W. Tao, N. Kong, X. Ji, et al., “Emerging two-dimensional monoelemental materials (Xenes) for biomedical applications,” *Chem. Soc. Rev.*, vol. 48, pp. 2891–2912, 2019, <https://doi.org/10.1039/c8cs00823j>.
 - [27] F. Xia, H. Wang, and Y. Jia, “Rediscovering black phosphorus as an anisotropic layered material for optoelectronics and electronics,” *Nat. Commun.*, vol. 5, pp. 4458, 2014, <https://doi.org/10.1038/ncomms5458>.
 - [28] M. Zhang, Q. Wu, F. Zhang, et al., “2D black phosphorus saturable absorbers for ultrafast photonics,” *Adv. Opt. Mater.*, vol. 7, pp. 1800224, 2019, <https://doi.org/10.1002/adom.201970001>.
 - [29] G. Qiu, Y. Wang, Y. Nie, et al., “Quantum transport and band structure evolution under high magnetic field in few-layer tellurene,” *Nano Lett.*, vol. 9, pp. 5760–5767, 2018.
 - [30] X. Huang, J. Guan, Z. Lin, et al., “Epitaxial growth and band structure of Te film on graphene,” *Nano Lett.*, vol. 17, pp. 4619–4623, 2017, <https://doi.org/10.1021/acs.nanolett.7b01029>.
 - [31] F. Zhang, G. Liu, Z. Wang, et al., “Broadband nonlinear absorption properties of two-dimensional hexagonal tellurene nanosheets,” *Nanoscale*, vol. 11, pp. 17058–17064, 2019, <https://doi.org/10.1039/C9NR03701B>.
 - [32] Y. Wang, G. Qiu, R. Wang, et al., “Field-effect transistors made from solution-grown two-dimensional tellurene,” *Nat. Electron.*, vol. 4, pp. 228–236, 2018, <https://doi.org/10.1038/s41928-018-0058-4>.
 - [33] L. Wu, W. Huang, Y. Wang, et al., “2D tellurium based high-performance all-optical nonlinear photonic devices,” *Adv. Funct. Mater.*, vol. 29, pp. 1705833, 2019, <https://doi.org/10.1002/adfm.201806346>.
 - [34] Z. Xie, C. Xing, W. Huang, et al., “Ultrathin 2D nonlayered tellurium nanosheets: facile liquid-phase exfoliation, characterization, and photoresponse with high performance and enhanced stability,” *Adv. Funct. Mater.*, vol. 26, pp. 1705833, 2018, <https://doi.org/10.1002/adfm.201705833>.
 - [35] J. Qiao, Y. Pan, F. Yang, C. Wang, Y. Chai, and W. Ji, “Few-layer tellurium: one-dimensional-like layered elementary semiconductor with striking physical properties,” *Sci. Bull.*, vol. 63, pp. 159–168, 2018, <https://doi.org/10.1016/j.scib.2018.01.010>.
 - [36] S. Gao, Y. Wang, R. Wang, and W. Wu, “Piezotronic effect in 1D van der Waals solid of elemental tellurium nanobelt for smart adaptive electronics,” *Semicond. Sci. Technol.*, vol. 32, pp. 104004, 2017, <https://doi.org/10.1088/1361-6641/aa8605>.
 - [37] Z. Gao, F. Tao, and J. Ren, “Unusually low thermal conductivity of atomically thin 2D tellurium,” *Nanoscale*, vol. 10, pp. 12997–13003, 2018, <https://doi.org/10.1039/C8NR01649F>.
 - [38] B. Yang, B. Wan, Q. Zhou, et al., “Te-doped black phosphorus field-effect transistors,” *Adv. Mater.*, vol. 28, pp. 9408–9415, 2016, <https://doi.org/10.1002/adma.201603723>.
 - [39] N. Antonatos, D. Bousa, S. Shcheka, S. M. Beladi-Mousavi, M. Pumera, and Z. Sofer, “In situ doping of black phosphorus by high-pressure synthesis,” *Inorg. Chem.*, vol. 58, pp. 10227–10238, 2019, <https://doi.org/10.1021/acs.inorgchem.9b01398>.
 - [40] Z. Zhang, M. Khurram, Z. Sun, and Q. Yan, “Uniform tellurium doping in black phosphorus single crystals by chemical vapor

- transport,” *Inorg. Chem.*, vol. 57, pp. 4098–4103, 2018, <https://doi.org/10.1021/acs.inorgchem.8b00278>.
- [41] T. Niu and A. Li, “From two-dimensional materials to heterostructures,” *Progress Surface Sci.*, vol. 90, pp. 21–45, 2015, <https://doi.org/10.1016/j.progsurf.2014.11.001>.
- [42] K. S. Novoselov, A. Mishchenko, A. Carvalho, and A. H. Castro Neto, “2D materials and van der Waals heterostructures,” *Science*, vol. 353, 2016, Art no. aac9439, <https://doi.org/10.1126/science.aac9439>.
- [43] D. Jariwala, T. J. Marks, and M. C. Hersam, “Mixed-dimensional van der Waals heterostructures,” *Nat. Mater.*, vol. 16, pp. 170–181, 2017, <https://doi.org/10.1038/nmat4703>.
- [44] M. Velický, and P. S. Toth, “From two-dimensional materials to their heterostructures: an electrochemist’s perspective,” *Appl. Mater. Today*, pp. 68–103, 2017, <https://doi.org/10.1016/j.apmt.2017.05.003>.
- [45] D. Chu, and E. K. Kim, “Recent advances in synthesis and assembly of van der Waals materials,” *J. Korean Phys. Soc.*, vol. 73, pp. 805–816, 2018, <https://doi.org/10.3938/jkps.73.805>.
- [46] V. Nicolosi, M. Chhowalla, M. G. Kanatzidis, M. S. Strano, and J. N. Coleman, “Liquid exfoliation of layered materials,” *Science*, vol. 340, pp. 1226419, 2013, <https://doi.org/10.1126/science.1226419>.
- [47] J. K. Dash, L. Chen, P. H. Dinolfo, T.-M. Lu, and G.-C. Wang, “A method toward fabricating semiconducting 3R-NbS₂ ultrathin films,” *J. Phys. Chem. C*, vol. 119, pp. 19763–19771, 2015, <https://doi.org/10.1021/acs.jpcc.5b04057>.
- [48] X. Sun, B. Zhang, Y. Li, et al., “Tunable uNonlinear optical properties of graphene/MoS₂ van der Waals heterostructures and their application in solid-state bulk lasers,” *ACS Nano*, vol. 12, pp. 11376–11385, 2018, <https://doi.org/10.1021/acsnano.8b06236>.
- [49] H. Mu, Z. Wang, J. Yuan, et al., “Graphene–Bi₂Te₃ heterostructure as saturable absorber for short pulse generation,” *ACS Photon.*, vol. 2, pp. 832–841, 2015, <https://doi.org/10.1021/acsphotonics.5b00193>.
- [50] X. Su, H. Nie, Y. Wang, et al., “Few-layered ReS₂ as saturable absorber for 2.8 μ m solid state laser,” *Opt. Lett.*, vol. 42, pp. 3502–3507, 2017, <https://doi.org/10.1364/OL.42.003502>.
- [51] Y. Zhang, D. Lu, H. Yu, and H. Zhang, “Low-dimensional saturable absorbers in the visible spectral region,” *Adv. Opt. Mater.*, vol. 7, pp. 1800886, 2019, <https://doi.org/10.1002/adom.201800886>.
- [52] Z. Sun, G.-H. Cheng, H. Liu, X. Wang, and Y.-G. Wang, “A single-longitudinal-mode passively Q-switched Nd:YVO₄ Laser using black phosphorus saturable absorber,” *Chin. Phys. Lett.*, vol. 1, pp. 61–64, 2017.
- [53] Z. Chu, J. Liu, Z. Guo, and H. Zhang, “2 μ m passively Q-switched laser based on black phosphorus,” *Opt. Mater. Expr.*, vol. 6, pp. 2374, 2016, <https://doi.org/10.1364/OME.6.002374>.
- [54] H. Nie, P. Zhang, B. Zhang, et al., “Watt-level continuous-wave and black phosphorus passive Q-switching operation of Ho³⁺,Pr³⁺:LiLuF₄ bulk laser at 2.95 μ m,” *IEEE J. Select. Top. Quant. Electron.*, vol. 5, pp. 1–5, 2018, <https://doi.org/10.1109/JSTQE.2017.2743047>.
- [55] J. Guo, J. Zhao, D. Huang, et al., “Two-dimensional tellurium-polymer membrane for ultrafast photonics,” *Nanoscale*, vol. 11, pp. 6235–6242, 2019, <https://doi.org/10.1039/C9NR00736A>.
- [56] N. Xu, P. Ma, S. Fu, et al., “Tellurene-based saturable absorber to demonstrate large-energy dissipative soliton and noise-like pulse generations,” *Nanophotonics* 2020, <https://doi.org/10.1515/nanoph-2019-0545>.
- [57] M. Hisyam, M. Rusdi, A. Latiff, and S. Harun, “Generation of mode-locked Ytterbium doped fiber ring laser using few-layer black phosphorus as a saturable absorber,” *IEEE J. Sel. Top. Quant.*, vol. 23, no. 99, pp. 1–5, 2016, <https://doi.org/10.1109/JSTQE.2016.2532270>.
- [58] H. Song Q. Wang. Y. Zhang, and L. Li, “Mode-locked ytterbium-doped all-fiber lasers based on few-layer black phosphorus saturable absorbers,” *Opt. Commun.*, vol. 394, pp. 157–160, 2017.
- [59] B. Zhang, F. Lou, R. Zhao, J. He, and J. Li, “Exfoliated layers of black phosphorus as saturable absorber for ultrafast solid-state laser,” *Opt. Lett.*, vol. 40, pp. 3691–3694, 2015, <https://doi.org/10.1364/OL.40.003691>.
- [60] X. Su, Y. Wang, B. Zhang, et al., “Femtosecond solid-state laser based on a few-layered black phosphorus saturable absorber,” *Opt. Lett.*, vol. 41, pp. 1945–1948, 2016, <https://doi.org/10.1364/OL.41.001945>.

Supplementary Material: The online version of this article offers supplementary material (<https://doi.org/10.1515/nanoph-2020-0174>).