Supplementary Information

Ultra-stable Pulse Generation in Ytterbium-Doped Fiber Laser Based on Black Phosphorus

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Electronic Supplementary Material (ESI) for Nanoscale Advances.
1. **Chemicals.**

Tetra-n-butyl-ammonium bisulfate (TBA·HSO$_4$, AR, 85%) was purchased from Aladdin. Red P (99.999%, CR), Dimethylformamide (DMF, 94.5-95%, AR), Acetone ((CH$_3$)$_2$CO, 99.5%, AR), and deoxygenated propylene carbonate were obtained from Sinopharm Chemical Reagent Co. Ltd. All chemicals were used directly without further purification. Milli-Q water with a resistivity higher than 18.2 M $\Omega$·cm$^{-1}$ was used in all preparations.

2. **Preparation of bulk black phosphorus crystal**

The high quality large-size bulk BP crystals were produced by mineralizer-assisted gas-phase transformation method. High pure red phosphorus (500 mg, chempur 99.999%) was enclosed in 200 mm long (inner-diameter: 8 mm) evacuated silica glass tubes as the precursor for growth. The tubes were placed in the heating zone of a quartz tube furnace. At first, the furnace was heated to 750 $^\circ$C (rate, 4 $^\circ$C/min) and holding for 1 h. After that, the sample was cooled to 500 $^\circ$C within 7.5 h and holding at this temperature in another 3 h. Finally, a slower cooling process to 150 $^\circ$C in 8 h was carried out, then the BP bulk crystals can be found after cooling down to room temperature.

3. **Characterization of black phosphorus saturable absorber**

Raman measurements were performed in a Horiba HR Evolution. The excitation was provided by visible laser light ($\lambda$= 473 nm) through a 100x objective. The Burker® Dimension ICON atomic force microscopy (AFM) was carried out to measure the thickness of the exfoliated BP samples. The Thermo Scientific ESCALAB 250Xi X-ray photoelectron spectroscopy (XPS) was used. Transmission electron microscopy (TEM) and high resolution TEM images were performed on an FEI Tecnai 20 (field-emission) scanning transmission electron microscope operating at 200 kV, equipped with an Oxford INCA X-sight EDS Si (Li) detector. The morphology of BP was observed by FEI Quanta 250 FEG scanning electron microscope and Hitachi S-4800 field emission scanning electron microscope.
4. **Sample preparation of black phosphorus saturable absorber**

The obtained BP-SA film was peeled off and transferred onto the fiber ferrule so that the fiber core was entirely covered, which can be seen in Fig. S 2. The fiber ferrule with the deposited BP-SA was then connected with a clean one via a fiber ferrule adapter, forming a SA ready for use in the fiber laser.

![Fig. S 1. The SEM image of BP vacuum filtration film.](image1)

![Fig. S 2. Digital image of a BP covered fiber ferrule.](image2)
5. Stability results

Fig. S3. Characteristics of the Q-switched pulse at 1μm for 4 hours in early 69 days: (a) optical spectrum of the laser; (b) central wavelength; (c) linewidth; (d) output power; (e) repetition rate and pulse duration. (a) and (b) shows that 1064.7 nm of central wavelength has hardly changed, which indicates that the spectrum was quite stable. The fluctuation of linewidth, output power, repetition rate and pulse duration from the average were less than 7.06%, 0.46%, 0.16% and 0.44%, respectively.
Fig. S 4. Characteristics of the Q-switched pulse at 1 μm for 4 hours in late 69 days: (a) optical spectrum of the laser; (b) central wavelength; (c) linewidth; (d) output power; (e) repetition rate and pulse duration. (a) and (b) shows that 1064.7 nm of central wavelength changed insignificantly, which indicates that the spectrum was quite stable. The fluctuation of linewidth, output power, repetition rate and pulse duration from the average were less than 3.24%, 0.27%, 0.63% and 0.25%, respectively.