

2 μm passively Q-switched laser based on black phosphorus

ZHAOZHENG CHU,¹ JIE LIU,^{1,*} ZHINAN GUO,² AND HAN ZHANG^{2,3}

¹Shandong Provincial Key Laboratory of Optics and Photonic Device, School of Physics and Electronics, Shandong Normal University, Jinan 250014, China

²SZU-NUS Collaborative Innovation Centre for Optoelectronic Science & Technology, and Key Laboratory of Optoelectronic Devices and Systems of Ministry of Education and Guangdong Province, College of Optoelectronic Engineering, Shenzhen University, China

³hzhang@szu.edu.cn

*jieliu@sdu.edu.cn

Abstract: Few-layer black phosphorus (BP) was successfully fabricated by liquid phase exfoliation (LPE) method. By using the BP saturable absorber (SA), a passively Q-switched solid-state laser at the central wavelength of 1988 nm was demonstrated. Under an absorbed diode-pumped power of 3.38 W, an average power of 151 mW was generated with a minimum pulse width of 1.78 μs and repetition rate of 19.25 kHz, corresponding to pulse energy of 7.84 μJ . Our experimental results showed that BP could be used as an excellent SA for achieving mid-infrared solid-state pulsed lasers. To the best of our knowledge, it was the first time to obtain a Q-switched solid-state laser of 2 μm based on BP-SA.

©2016 Optical Society of America

OCIS codes: (140.3380) Laser materials; (140.3580) Lasers, solid-state; (140.3540) Lasers, Q-switched.

References and links

1. A. V. Podlipensky, V. G. Shcherbitsky, N. V. Kuleshov, V. I. Levchenko, V. N. Yakimovich, M. Mond, E. Heumann, G. Huber, H. Kretschmann, and S. Kück, "Efficient laser operation and continuous-wave diode pumping of $\text{Cr}^{2+}:\text{ZnSe}$ single crystals," *Appl. Phys. B* **72**(2), 253–255 (2001).
2. L. Wu, D. Li, S. Zhao, K. Yang, X. Li, R. Wang, and J. Liu, "Passive Q-switching with GaAs or Bi-doped GaAs saturable absorber in Tm:LuAG laser operating at 2 μm wavelength," *Opt. Express* **23**(12), 15469–15476 (2015).
3. J. Hou, B. T. Zhang, X. C. Su, R. W. Zhao, Z. W. Wang, F. Lou, and J. L. He, "High efficient mode-locked Tm:YAP laser emitting at 1938 nm by SESAM," *Opt. Commun.* **347**, 88–91 (2015).
4. M. A. Watson, M. V. O'Connor, D. P. Shepherd, and D. C. Hanna, "Synchronously pumped CdSe optical parametric oscillator in the 9–10 microm region," *Opt. Lett.* **28**(20), 1957–1959 (2003).
5. S. H. Kassani, R. Khazaeizhad, H. Jeong, T. Nazari, D. I. Yeom, and K. Oh, "All-fiber Er-doped Q-Switched laser based on Tungsten Disulfide saturable absorber," *Opt. Mater. Express* **5**(2), 373–379 (2015).
6. B. Chen, X. Zhang, K. Wu, H. Wang, J. Wang, and J. Chen, "Q-switched fiber laser based on transition metal dichalcogenides MoS_2 , MoSe_2 , WS_2 , and WSe_2 ," *Opt. Express* **23**(20), 26723–26737 (2015).
7. F. Bonaccorso, Z. Sun, T. Hasan, and A. C. Ferrari, "Graphene photonics and optoelectronics," *Nat. Photonics* **4**(9), 611–622 (2010).
8. H. Zhang, D. Y. Tang, L. M. Zhao, Q. L. Bao, and K. P. Loh, "Large energy mode locking of an erbium-doped fiber laser with atomic layer graphene," *Opt. Express* **17**(20), 17630–17635 (2009).
9. X. L. Qi and S. C. Zhang, "Topological insulators and superconductors," *Rev. Mod. Phys.* **83**(4), 1057–1110 (2011).
10. H. Zhang, S. B. Lu, J. Zheng, J. Du, S. C. Wen, D. Y. Tang, and K. P. Loh, "Molybdenum disulfide (MoS_2) as a broadband saturable absorber for ultra-fast photonics," *Opt. Express* **22**(6), 7249–7260 (2014).
11. C. Lee, X. Wei, J. W. Kysar, and J. Hone, "Measurement of the elastic properties and intrinsic strength of monolayer graphene," *Science* **321**(5887), 385–388 (2008).
12. A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, and A. K. Geim, "The electronic properties of graphene," *Rev. Mod. Phys.* **81**(1), 109–162 (2009).
13. K. I. Bolotin, K. J. Sikes, Z. Jiang, M. Klima, G. Fudenberg, J. Hone, P. Kim, and H. L. Stormer, "Ultrahigh electron mobility in suspended graphene," *Solid State Commun.* **146**(9–10), 351–355 (2008).
14. A. A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao, and C. N. Lau, "Superior thermal conductivity of single-layer graphene," *Nano Lett.* **8**(3), 902–907 (2008).
15. S. Yan, B. Wang, Z. Wang, D. Hu, X. Xu, J. Wang, and Y. Shi, "Supercritical carbon dioxide-assisted rapid synthesis of few-layer black phosphorus for hydrogen peroxide sensing," *Biosens. Bioelectron.* **80**, 34–38 (2016).
16. Z. Qin, G. Xie, H. Zhang, C. Zhao, P. Yuan, S. Wen, and L. Qian, "Black phosphorus as saturable absorber for

- the Q-switched Er:ZBLAN fiber laser at 2.8 μm ,” *Opt. Express* **23**(19), 24713–24718 (2015).
17. B. Zhang, F. Lou, R. Zhao, J. He, J. Li, X. Su, J. Ning, and K. Yang, “Exfoliated layers of black phosphorus as saturable absorber for ultrafast solid-state laser,” *Opt. Lett.* **40**(16), 3691–3694 (2015).
 18. H. Yu, X. Zheng, K. Yin, X. A. Cheng, and T. Jiang, “Nanosecond passively Q-switched thulium/holmium-doped fiber laser based on black phosphorus nanoplatelets,” *Opt. Mater. Express* **6**(2), 603–609 (2016).
 19. Y. Chen, G. Jiang, S. Chen, Z. Guo, X. Yu, C. Zhao, H. Zhang, Q. Bao, S. Wen, D. Tang, and D. Fan, “Mechanically exfoliated black phosphorus as a new saturable absorber for both Q-switching and Mode-locking laser operation,” *Opt. Express* **23**(10), 12823–12833 (2015).
 20. J. Sotor, G. Sobon, M. Kowalczyk, W. Macherzynski, P. Paletko, and K. M. Abramski, “Ultrafast thulium-doped fiber laser mode locked with black phosphorus,” *Opt. Lett.* **40**(16), 3885–3888 (2015).
 21. Y. Takao, H. Asahina, and A. Morita, “Electronic structure of black phosphorus in tight binding approach,” *J. Phys. Soc. Jpn.* **50**(10), 3362–3369 (1981).
 22. V. Tran, R. Soklaski, Y. F. Liang, and L. Yang, “Layer-controlled band gap and anisotropic excitons in few-layer black phosphorus,” *Phys. Rev. B* **89**(23), 235319 (2014).
 23. S. B. Lu, L. L. Miao, Z. N. Guo, X. Qi, C. J. Zhao, H. Zhang, S. C. Wen, D. Y. Tang, and D. Y. Fan, “Broadband nonlinear optical response in multi-layer black phosphorus: an emerging infrared and mid-infrared optical material,” *Opt. Express* **23**(9), 11183–11194 (2015).
 24. F. Xia, H. Wang, and Y. Jia, “Rediscovering black phosphorus as an anisotropic layered material for optoelectronics and electronics,” *Nat. Commun.* **5**, 4458–4463 (2014).
 25. Z. Wang, R. Zhao, J. He, B. Zhang, J. Ning, Y. Wang, X. Su, J. Hou, F. Lou, K. Yang, Y. Fan, J. Bian, and J. Nie, “Multi-layered black phosphorus as saturable absorber for pulsed Cr:ZnSe laser at 2.4 μm ,” *Opt. Express* **24**(2), 1598–1603 (2016).
 26. Y. Akahama, M. Kobayashi, and H. Kawamura, “Raman study of black phosphorus up to 13 GPa,” *Solid State Commun.* **104**(6), 311–315 (1997).
 27. A. C. Gomez, L. Vicarelli, E. Prada, J. O. Island, K. L. N. Acharya, S. I. Blanter, D. J. Groenendijk, M. Buscema, G. A. Steele, J. V. Alvarez, H. W. Zandbergen, J. J. Palacios, and H. S. J. Zant, Isolation and characterization of few-layer black phosphorus, *2D Mater.* **1**(2), 025001 (2014).

1. Introduction

Pulsed laser sources are powerful research tools for many scientific research fields. Mid-infrared Q-switched lasers, especially the pulsed lasers centered at a spectral wavelength of 2 μm with high compactness and great efficiency have attracted much attention [1, 2]. The traditional ways to achieve pulsed lasers are passively Q-switched techniques based on different materials as saturable absorbers (SAs) [3–5]. In recent years two-dimensional (2D) materials as a new kind of SA bring new opportunities for pulsed laser. 2D materials such as graphene, the insulating hexagonal boron nitride (hBN), the transition metal dichalcogenides (TMDCs), and the topological insulators (TIs) have been widely investigated and applied as SAs [6–10] because of their outstanding mechanical [11], electrical [12], carrier transport [13], and thermal properties [14] in association with other outstanding physical and chemical properties.

Lately, black phosphorus (BP), a new two dimensional (2D) material, has attracted great attention as saturable absorber (SA) [15–20]. Different from semi-metallic graphene and wide transition-metal dichalcogenides, BP has a direct band-gap for all thickness [from 0.3 eV (bulk) to 2.0 eV (monolayer)] which makes it possible to control the direct band gap of BP by changing the number of stacked layers [21–24]. Further-more, the inter-band optical absorption of multilayer BP could be readily saturated under strong illumination of mid-infrared lasers. For these reasons, the applications of BP as a new kind of SA are irreplaceable at the mid-infrared part of the spectrum by other 2D layer materials. Using BP-SAs, Q-switched pulses of 1.5 μm [19], 2 μm [18], 2.4 μm [25] and 2.8 μm [16] have been generated from the fiber lasers. However, most of the Q-switched operations with black phosphorus were limited to fiber laser. No solid-state format of Q-switched laser was reported at 2 μm wavelength based on BP-SAs so far.

In this paper, a Q-switched solid-state laser of 2 μm was successfully obtained with high quality BP employed as SA for the first time. Experiments were realized in a simple linear cavity using two output couplers of different transmissions. Under an absorbed pump power of 3.38 W and an output coupling ratio of 2%, the passive Q-switched laser with a maximum average output power of 151 mW, the pulse width of 1.78 μs and the repetition rate of 19.25

kHz had been obtained, corresponding to pulse energy of 7.84 μJ . With an output coupling ratio of 5%, the maximum average output power of Q-switched laser was 207 mW at an absorbed pump power of 4.04 W. The minimum pulse width was 2.25 μs and the pulse repetition rate was 17.21 kHz, leading to pulse energy of 12.07 μJ . Comparison between our laser and the 2- μm fiber laser reported before (maximum pulse energy of 632.4 nJ, shortest pulse width of 731 ns and pulse repetition of 113.3 kHz) showed that the laser pulse energy of our device was far greater. Our work demonstrated that multilayer BP was a competitive material as SA in mid-IR pulses laser.

2. Experimental setup

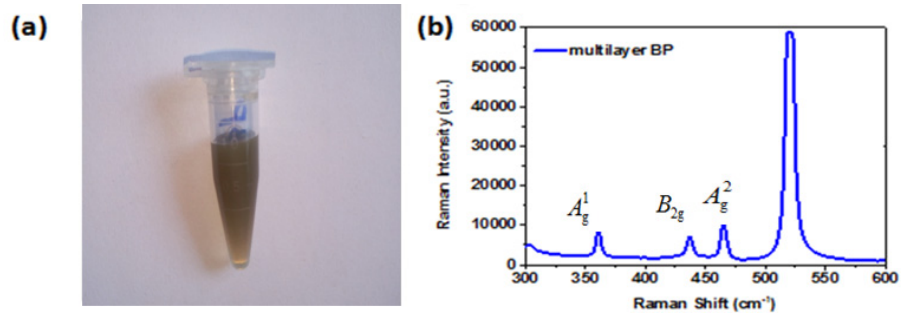


Fig. 1. Photograph of multilayer BP dispersed in NMP and Raman spectra of few-layered BP.

The BP powder was dissolved using N-methylpyrrolidone (NMP) as solvent. Then the mixture was ultrasonically agitated for about 40 min. Figure 1(a) shows that after ultrasonication the black phosphorus (BP) powder was evenly distributed in the N-methylpyrrolidone (NMP) solution. Then, the solution was dropped onto the center of the quartz plate and centrifuged at 1500 r/min for several times in order to evenly coat on the plate. After that, the sample was placed in a vacuum box to dry naturally. Figure 1(b) depicts the Raman spectra of the as-prepared sample. As we can see, in addition to a Raman peak of silicon at 520.7 cm^{-1} , there were three other main Raman peaks of A_g^1 , B_{2g} and A_g^2 located at 361 cm^{-1} , 437 cm^{-1} and 465 cm^{-1} . The A_g^1 mode was caused by the out-of-plane vibration of phosphorus atoms and the B_{2g} and A_g^2 modes originated from the in-plane oscillation of phosphorus atoms [26]. Figure 2 displays the atomic force microscope (AFM) scan image of the BP on the quartz plate. We can see the morphology of the multilayer BP that has a diameter of 200 nm and a variable thickness from 3 nm to 8 nm. It is well known that single layer of BP is about 0.6 nm in thickness [24, 27], which suggests that the layer number of the as-fabricated BP sheets in our experiments varies from 5 to 13. The transmission was measured to be 95% by the 2- μm continuous-wave (CW) laser.

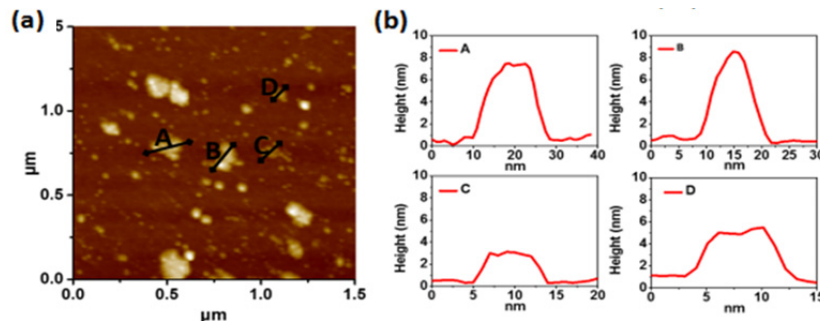


Fig. 2. AFM scan image of the BP surface and the typical height profiles of BP sheets.

A fiber-coupled CW diode laser of 795 nm (fiber core diameter of 400 μm and numerical aperture of 0.22) was employed as the pumping source. A 5 at.-%-doped Tm:YAP crystal was selected as the laser gain medium with the dimension of 3mm \times 3mm \times 4mm. By an optics coupling system of 1:0.8, the pump beam was focused into the crystal. The crystal was wrapped with indium foil and placed in a Cu holder of 14 $^{\circ}\text{C}$ cooled by water. A 43-mm straight concave-plane cavity composed of a concave mirror (M1) and a plane mirror (M2) was constructed. M1 was AR-coated for 795 nm and HT-coated for the spectral range of 1900–2000 nm with a radius of 100 mm. M2 was a plane mirror with different transmissions of 2% and 5% for the spectral range of 1900–2000 nm. The diameter of laser spot size focused on M2 was calculated to be 105 μm with the propagation ABCD matrix theory. The BP was placed into the cavity close to the output coupler and stable Q-switched pulses were obtained after accurately aligning the mirrors.

As it is well-known, BP is easily oxidized in the air and water molecules have a strong absorption of light near 2 μm . In order to minimize the impact of these phenomena on our experiments, we strictly controlled both temperature and air humidity of our laboratory.

3. Experiment results and discussion

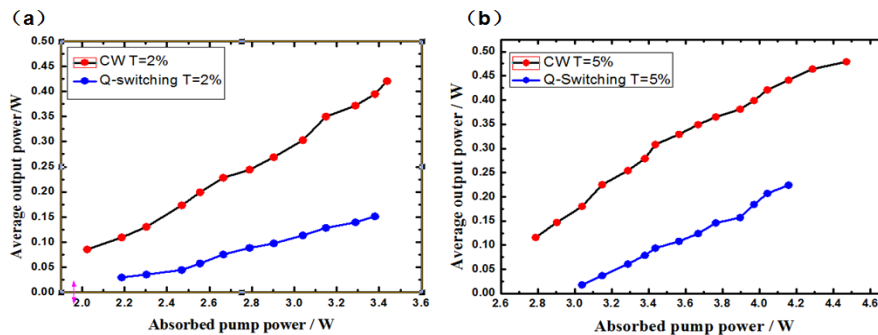


Fig. 3. Output power versus pump power for CW and Q-switched operation.

Figure 3(a) shows the dependence of the average output power on the absorbed power, measured with the output coupler of 2% transmission. The maximum average output power of CW laser was 395 mW at a pumped power of 3.38 W, measured by the power meter (30A-SH-V1, Israel). The slope indicates an efficiency of 23.5%. With the BP-SA employed in the cavity, the maximum average output power of the stable Q-switched laser was 151 mW and the slope (or efficiency) was 10.7%. When the transmission of output coupler was 5%, the results are shown in Fig. 3(b). The maximum average output powers of CW laser and the stable Q-switched laser were 441 mW and 207 mW at the pump power of 4.04 W, corresponding to the efficiencies of 23% and 17.6%, respectively. As we continued to increase the pump power, the passive Q-switched operation started to become unstable in both experiments.

We performed an experiment on the stability of the Q-switched operation by continuous monitoring of the output power for an hour. The fluctuation in the output power was measured to be less than 15%. There was no damage to the sample during the entire stable Q-switched operation. We believe that the saturation effect of the absorber should render the unstability of the Q-switched waves. Then, to accurately measure the laser damage threshold of our BP-SAs, we increased the pump power; and found that stable Q-switched operation disappeared at the absorbed pump power of 3.38 W. The BP-SA was destroyed visible to the naked eye under absorbed pump power of 5.06 W. The average output power was measured to be 327 mW and the power density close to the output coupler was calculated to be 41.67 kW/cm^2 . We reduced the pump power and could not achieve a Q-switched operation anymore and the BP sample was determined to be damaged. Next, we shifted the BP sample laterally

so that the CW laser beam was shone on a different position of the BP sample; and stable Q-switched pulses were re-obtained after alignment of the mirrors.

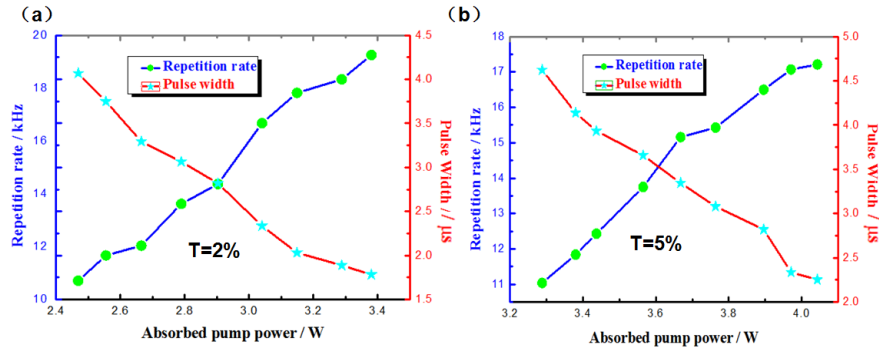


Fig. 4. Pulse repetition rate and pulse width versus the absorbed pump power.

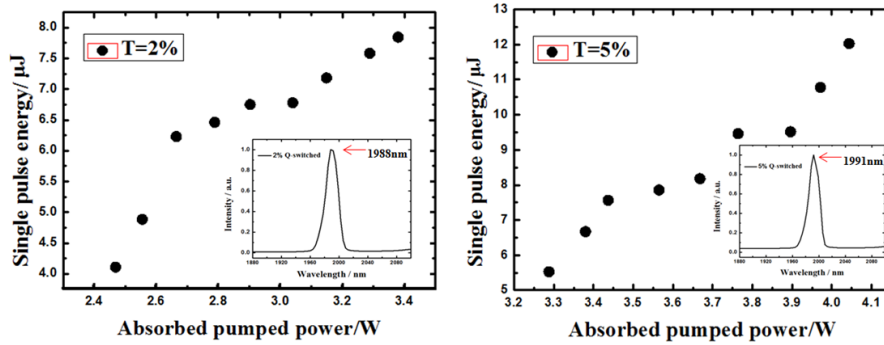


Fig. 5. The single pulse energy versus the absorbed pump power and the output spectra of passively Q-switched operation.

The dependence of the pulse width and the pulse repetition rate to the absorbed pump power is shown in Fig. 4. The pulse width became narrower and the repetition frequency increased with the increase of the pump power in both experiments. At the output coupler of 2% transmission, the generated Q-switched pulses had a highest repetition rate of 19.25 kHz and a shortest pulse width of 1.78 μ s, corresponded to a pulse energy of 7.84 μ J. With the output coupler transmission being 5%, the shortest pulse width was 2.25 μ s and the highest pulse repetition rate was 17.21 kHz, leading to a pulse energy of 12.03 μ J. The Q-switched laser spectra were measured to be 1988 nm ($T = 2\%$) and 1991 nm ($T = 5\%$) by an optical spectrum analyzer (AvaSpec-NIR256-2.2-RM). The pump-power-dependent output pulse energies and output spectra of passively Q-switched operation are shown in Fig. 5. The typical oscilloscope pulse trains of the both experiments (with the narrowest pulse widths) are displayed in Fig. 6. The corresponding oscilloscope traces were measured by a fast photodiode (EOT ET-5000) and a digital oscilloscope (Tektronix DPO4054, USA). It is clear to see that the amplitude of the pulse sequence fluctuates within the range of 15%.

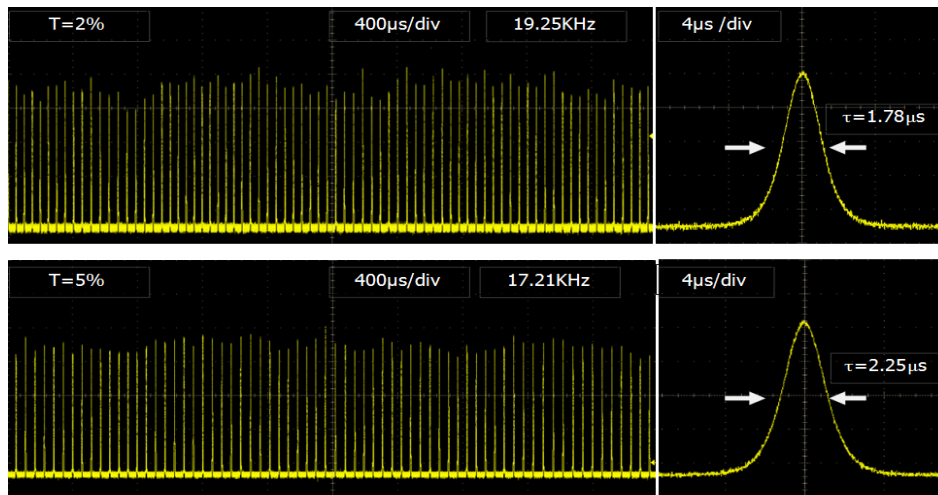


Fig. 6. Typical pulse trains of the Q-switched laser in different time scales.

4. Conclusions

A compact stable passively Q-switched solid-state laser enabled with BP-SA at $2\mu\text{m}$ had been demonstrated for the first time. When the transmission of output mirror was 2%, the shortest pulse width and highest pulse repetition rate were measured to be $1.78\mu\text{s}$ and 19.25kHz , respectively. The maximum output power was 151mW , corresponding to a single-pulse energy of $7.84\mu\text{J}$. At the output mirror transmission of 5%, the shortest pulse width and highest pulse repetition rate were measured to be $2.25\mu\text{s}$ and 17.21kHz , respectively. The average output power was 207mW with the single pulse energy of $12.03\mu\text{J}$. BP had been verified to be an excellent material as SA for generation of mid-infrared laser pulses. Our experimental results are expected to be further improved with better output performance if higher quality BP samples are fabricated.

Funding

National Natural Science Foundation of China (61475089 and 61435010); Science and Technology Development Projects of Shandong Province (2013GGX10108); The Science and Technology Innovation Commission of Shenzhen (KQTD2015032416270385 and JCYJ20150625103619275).