Electronic structures and NIR-II optical properties of black phosphorus using first principles*

HONG Xiaofeng[1], GUO Meili[2], LIU Ling[3], LI Yonghui[4], and ZHANG Xiaodong[3,4]**

1. *Science and Technology on Reactor Fuel and Materials Laboratory, Nuclear Power Institute of China, Chengdu 610041, China*
2. *Department of Physics, School of Science, Tianjin Chengjian University, Tianjin 300384, China*
3. *Tianjin Key Laboratory of Brain Science and Neural Engineering, Academy of Medical Engineering and Translational Medicine, Tianjin University, Tianjin 300072, China*
4. *Department of Physics and Tianjin Key Laboratory of Low Dimensional Materials Physics and Preparing Technology, School of Sciences, Tianjin University, Tianjin 300350, China*

(Received 9 May 2022; Revised 9 June 2022)

Near infrared-II (NIR-II, 1 000—1 700 nm) imaging with high penetration tissue depth and signal-noise ratio has attracted wide interest in biomedicine. As a two-dimensional (2D) material with narrow band gap, the band structure of layered black phosphorus, as an important characteristic of electronic structure, determines the electronic transport and infrared optical properties, which show great potential in NIIR-II imaging. Here, the electronic structure and NIR-II optical properties of black phosphorus have been investigated in detail by employing the generalized gradient approximation + U (GGA+U) correction based on density functional theory (DFT). First, we performed the band structure and density of states for different layers of black phosphorus. From the electronic structures, the location of valence band maximum didn't shift obviously, and the position of conduction band minimum shifted downward gradually, inducing the band gaps decreased gradually with the increasing layer number. While the layer number increased to 5, the behaviour of electronic structure was very similar to that of the bulk black phosphorus. Then, we calculated the NIR-II optical properties, and found the optical band gap of black phosphorus also showed layer dependent properties. From a single layer to 5 layers, the optical band gap changed from 1.71 eV to 0.92 eV. It is noting that black phosphorus also showed the significant optical absorption in NIR-IIa (1 300—1 400 nm) and NIR-IIb (1 500—1 700 nm) windows. Especially, the NIR-II optical absorption can be enhanced with increasing the layer number to 5, indicating promising photoresponse materials in NIR-II imaging.

Document code: A **Article ID:** 1673-1905(2022)10-0595-6

DOI https://doi.org/10.1007/s11801-022-2077-7

Due to high tissue penetration and improved imaging quality, the near infrared-II (NIR-II, 1 000—1 700 nm) imaging has received wide attention[1,2]. Compared with traditional near infrared-I (NIR-I, 750—900 nm) window, NIR-II imaging shows the wavelength dependent decreasing scattering, leading to increasing tissue penetration depth up to centimeter level. The powerful imaging capability allows it to achieve the high resolution imaging in tumor tracking[1], brain imaging[2], as well as blood vessel related disease diagnosis. NIR-II imaging, however, always requires the highly bright and small band gap direct semiconductor[3]. Unfortunately, lots of semiconductor materials, such as CdS, CdSe, CdTe ZnO, ZnS, show larger band gap (>2 eV) and visible optical transition, failure to emitting NIR-II light. Thus, it is desirable to explore other small gap materials for NIR-II imaging.

Two-dimensional (2D) materials, such as graphene and MoS_2, hold the small band gap, attracting tremendous research interests[4,5]. They exhibit superior mechanical, electrical, and optical properties over their bulk counterparts. Graphene has an excellent carrier mobility and toughness. However, it doesn't present property of semiconductor, which limits its applications. Unlike graphene, single layer MoS_2 possesses a direct band gap, promising for light emitter, photoelectric detector, and even the solar cell. Unfortunately, MoS_2 has a relatively low carrier mobility of ~200 $cm^2 \cdot V^{-1} \cdot s^{-1}$, improvable up to 500 $cm^2 \cdot V^{-1} \cdot s^{-1}$, which is far away from actual application requirements[5].

* This work has been supported by the National Natural Science Foundation of China (Nos.81971744, U1932107, 91859101, and 11304220), and the Natural Science Foundation of Tianjin (Nos.2021FJ-0009 and 19JCZDJC34000).
** E-mail:meiliguo314@163.com

Recent years, a promising 2D material, black phosphorus, has been successfully fabricated[6,7]. It was mechanical exfoliated from black phosphorus. Phosphorus has four allotropes, among which black phosphorus is the most stable allotrope at room temperature. It was synthesized firstly from red phosphorus under high pressure and high temperature in 1914. Similar to graphite, its layered structure is held together by weak interlayer forces with significant van der Waals character. Inside a single layer, each phosphorus atom is covalently bonded with three adjacent phosphorus atoms to form a puckered honeycomb structure (Fig.1(a)). Excitingly, black phosphorus not only has a direct band gap like monolayer MoS_2, but also has a high carrier mobility, and the mobility is found to be thickness-dependent with the highest value up to ~1 000 $cm^2 \cdot V^{-1} \cdot s^{-1}$ obtained for a thickness of ~10 nm. In particular, the layer-dependent band gap black phosphorus leads to its broad optical absorption across ultra-violet (UV), infrared and visible light spectra, which makes it an ideal candidate for use in photothermal therapy, biosensing, photoacoustic imaging, and drug delivery. The high ON-OFF current ratio of black phosphorus can be widely used in field effect transistor-based immunosensors to detect antigen or antibody with high sensitivity based on the electrical resistance measurement. These properties make black phosphorus an ideal 2D material for device, as well as potential optical materials in NIR-II window[8]. A number of studies have been performed to understand the electronic properties of monolayer and few-layer black phosphorus. KUTLU et al[9] investigated the electronic and optical properties of black phosphorus doped with Au, Sn and I atoms. KUMAWAT et al[10] have explored the structural, electronic, adsorption, and quantum transport properties of phosphorene nanoribbon in the presence of different nitroaromatic compounds using the state-of-the-art first-principle density functional theory (DFT) calculations. Furthermore, black phosphorus also presents strong anisotropic properties in the mid-infrared region and electronic properties within the plane of the layers, which is obviously different from graphene and MoS_2[11]. However, the optical properties of few-layer black phosphorus in NIR-II window by DFT have rarely been studied.

In this study, we investigate the detailed electronics states and NIR-II optical transition of black phosphorus, which are crucial to NIR-II imaging. Herein, we calculated the layer dependent electronic structures and NIR-II optical properties of black phosphorus based on the DFT. First, we built the models of bulk black phosphorus and few-layer black phosphorus. Second, generalized gradient approximation + U (GGA+U) correction was performed for the bulk black phosphorus and single layer black phosphorus to obtain accurate band gap relative to the experimental value. Third, we calculated the energy band structure and density of states of different layers. Last, we presented the imaginary part of dielectric function and NIR-II absorption properties of different layers.

The calculations are performed with Vienna ab-initio simulation package (VASP) code based on DFT using a plane-wave pseudo potential method[12]. Under the GGA[13], the exchange-correlation energy was described with the Perdew-Burke-Ernzerhof (PBE) function. Electron-ion interactions were described by norm-conserving pseudopotential[14]. The electronic state $3s^2 3p^3$ was considered as the valence state for P atoms. The cutoff energy for the plane-wave basis was set to 500 eV for the different layers of black phosphorus.

Firstly, geometry optimization was performed for different few-layer black phosphorus. The equilibrium lattice constants and atomic positions were deduced from the total-energy minimization by using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) geometry optimization method. Relaxations of the lattice parameters and atomic positions were carried out under the constraint of the unit-cell space group symmetry. Energy-volume relations were obtained by varying unit-cell volume and the fitting results were obtained using the Murnaghan equation of state as

$$E_{\mathrm{tol}} = \frac{B_0 V}{B_0'}\left[\left(\frac{V_0}{V}\right)^{B_0'}\left(\frac{1}{B_0'-1}\right)+1\right]+E_0. \tag{1}$$

According to the fitting results, the estimated value of the static bulk modulus B_0 at zero pressure and the first-order pressure derivative of the bulk modulus B_0' were obtained. In the optimization process, the energy tolerance, tolerance of the force, maximum stress and maximum displacement were set as 1×10^{-5} eV/atom, 0.03 eV/Å, 0.05 GPa and 0.001 Å, respectively.

We used the U correction to improve the band gaps of bulk black phosphorus and different layers of black phosphorus for underestimating the band gap by GGA method. Different U values from 2 eV to 7 eV were tested, and we found that 6 eV was appropriate by comparing with the experimental results. And then, the electronic structures and optical properties of phosphorus with different layers were performed using GGA+U method. All parameters here, such as k-point and cutoff energy, were the same as the structure optimization.

To explore the electronic structures and optical properties of black phosphorus with different layers, 2×2×3 periodically repeated supercells were employed, which contained 16, 32, 48, 64, and 80 atoms, corresponding to the 1 to 5 layers, respectively. A vacuum space of 20 Å was used to avoid the interaction between periodic images.

For the bulk black phosphorus (Fig.1(a)), inside a single layer, each phosphorus atom is covalently bonded with three adjacent phosphorus atoms to form a puckered honeycomb structure. The lattice constants of bulk black phosphorus are a=3.31 Å, b=4.38 Å, and c=10.50 Å, respectively, which is consistent with the previous report[6]. In order to investigate the layer-dependent electronic structures and optical properties of black phosphorus, we built the layer-dependent geometry structures

from 1 to 5 layers. In Fig.1(b) and Fig.1(c), we present the structures of single layer black phosphorus from top view and side view, respectively.

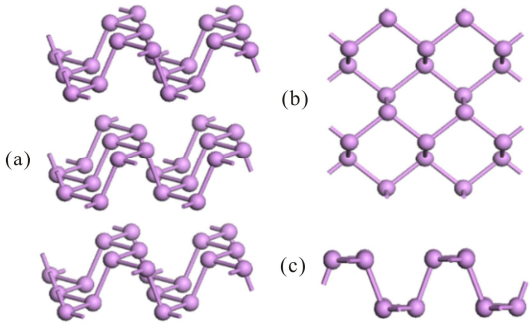


Fig.1 Geometry structures of (a) bulk black phosphorus and single layer black phosphorus with (b) top view and (c) side view

We optimized the geometry structures of black phosphorus and black phosphorus with few layers which were fully relaxed according to the force and stress calculated by DFT. The lattice constants of optimized structures of bulk and few-layer black phosphorus were presented in Tab.1. After relaxation, the lattice constants of the bulk black phosphorus changed to be a=3.234 Å and b=4.501 Å, respectively, which changed a little compared to the pristine structure and consistent with previous experimental results[15]. For the different layers, the constant a was gradually increased to 3.323 Å with the increasing layer number, and the constant b was increased overall compared to the bulk. The lattice parameters of single layer were corresponding to a=3.251 Å and b=4.686 Å, which are very close to other researches, indicating that the calculation results are reliable. In addition, we also compared the change of bond length. There are three bonds for every P atom, among which, the length of long bond was 2.203 Å, and that of the short bond was 2.168 Å for the bulk system. After relaxation, the bond lengths changed to 2.235 Å and 2.191 Å, respectively. The bond lengths of single layer were 2.218 Å and 2.197 Å after relaxation. GOMEZ et al also relaxed the single layer black phosphorus based on the DFT, and they obtained the bond lengths of 2.207 Å and 2.164 Å, respectively, which are similar to our results. These results indicated that the lattice constants had a little change after relaxation and our results are reliable.

Owing to the inaccurate description of the electron-electron exchange interaction of the GGA approach, the conventional DFT function usually predicts a much smaller band gap than the experimentally obtained band gap. In our study, when we used the GGA method, the band gap of bulk black phosphorus was 0.14 eV, and that of the single layer black phosphorus was 0.84 eV, which were both lower than the experiment values[6,7]. To better describe the exchange interaction, the band structures for bulk black phosphorus and few-layer black phosphorus were calculated by using GGA+U method. U value was added to p states of P atom. In order to choose suitable U value and ensure the reliability of result, we performed the band gap calculations of bulk phosphorus and single layer black phosphorus with different U values from 2 eV to 7 eV, which were presented in Fig.2. It was found that the band gap of bulk black phosphorus increased from 0.16 eV to 0.40 eV corresponding to the U value from 2 eV to 7 eV. Similarly, the band gap of single layer black phosphorus was increased with the increasing U value. The single layer black phosphorus gap was in the range from 0.94 eV to 1.29 eV, corresponding to the U value from 2 eV to 7 eV. It was revealed that the band gap of single layer black phosphorus was larger than that of bulk black phosphorus. Compared with experiment results, we could confirm that appropriate U value is 6 eV. In this case, the band gap of bulk black phosphorus increased up to 0.33 eV, which is consistent with the experimental value[16]. While the band gap of single layer black phosphorus increased to 1.21 eV, which is consistent with the experimental value and other theoretical reports[7]. LIU et al[7] reported that single layer black phosphorus had a direct band gap of 1.0 eV at Gamma, and the calculated band gap value for the bulk system was E_g=0.31 eV, which was close to our result. It was also reported that the band structure of single layer black phosphorus used hybrid function, such as Heyd-Scuseria-Ernzerhof (HSE06) and PBE methods, which was about 1.52 eV and 0.84 eV, respectively. Other researchers also showed the band gap of bulk black phosphorus was 0.31—0.36 eV[17]. Thus, it is feasible to use the GGA+U method to calculate the electronic and optical properties of few-layer black phosphorus. In the following calculations of electronic structures and optical properties, we used the GGA+U method to investigate the different black phosphorus systems.

Tab.1 Lattice constants of bulk and few-layer black phosphorus

	a (Å)	b (Å)
Bulk	3.234	4.501
1 layer	3.251	4.686
2 layers	3.253	4.642
3 layers	3.318	4.619
4 layers	3.321	4.599
5 layers	3.323	4.619

Next, we move to the energy band structure. Fig.3 presents the band structures of bulk system and black phosphorus with different layers from 1 to 5. It was found that both the valance band maximum (VBM) and conduction band minimum (CBM) were located at high symmetric G point for both bulk and few layers systems, indicating the nature of the direct band gap materials. In contrast, MoS_2 presents a conversion from direct band gap to indirect band gap when increasing layer number

from monolayer to bulk[18], which means it is more difficult to absorb or emit electrons efficiently through interband transitions, limiting the application in photoelectric field of MoS_2. By comparing the band structures, we found that the positions of VBM with respect to the Fermi level had no obvious shift, while the CBM shifted to the low energy obviously, which induced the band gap narrowing with the increasing layer number. When the layer number increased to 5, the band gap was close to that of bulk phosphorus. The differences in the electronic structure between bulk and few-layer black phosphorus may originate only from Van der Waals interaction. By using U correction, the band gap of bulk system was enlarged to 0.33 eV compared to the DFT band gap of 0.08 eV, which was consistent with other reports[19]. For the few-layer black phosphorus, the band gap depended sensitively on the number of layers. When the number of layers was 1, the band gap was 1.21 eV. With the increasing layer number, the band gap decreased to 0.79 eV, 0.62 eV, 0.51 eV and 0.49 eV, corresponding to 2, 3, 4 and 5 layers. This indicated that band gap was tunable in a wide range. Previous first-principles calculations also showed that the band gap ranged from ~1.5 eV for a single layer to ~0.6 eV for the 5-layer. SAPTARSHI et al obtained the band gap of bilayer black phosphorus about to be 0.72 eV experimentally, which was close to 0.79 eV in this work. TRAN et al calculated the band gap of black phosphorus with different layers using three methods and the result showed that the band gaps of single layer were 2.0 eV, 1.18 eV and 0.85 eV, corresponding to the GW, Bethe-Salpeter equation (BSE), and DFT methods, and the band gap of bulk system was 0.3 eV by using GW and BSE methods.

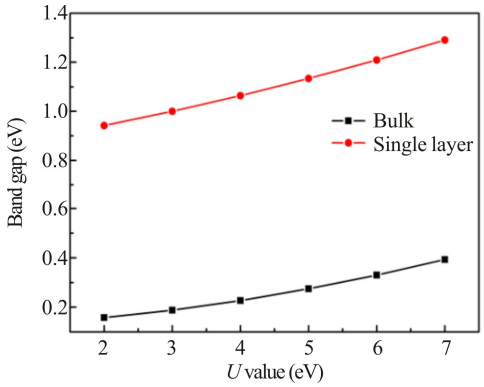


Fig.2 Band gaps of bulk phosphorus and single layer black phosphorus with different *U* values

Density of states (*DOS*) is another concern for the few-layer black phosphorus. Fig.4 presents the *DOS* of black phosphorus with different layers. The valence band and conduction band mainly consisted of the 3p and 3s states of P atom. In the uppermost valence band and lowest conduction band, 3p states of P were predominantly found, while the 3s states were relatively few. In addition, some delocalized states of uppermost valence band were formed in different layers of black phosphorus, which located mainly in the range from −1 eV to 0 eV. For the single layer, the delocalization was most significant, which is consistent with the band structure result. In the band structure of single layer, the delocalized states located in −2—0 eV (Fig.3). With the layer number increased, delocalization gradually turned to be weak. When the layer number is up to 5, the delocalized states mixed with uppermost valence band. In addition, from 1 to 5 layers, the uppermost valance band didn't shift obviously, and the lowest conduction band shifted gradually to the lower energy region. The lowest conduction band of single layer black phosphorus was 1.51 eV, while for the 5 layers black phosphorus, the lowest conduction band shifted obviously to 0.4 eV, inducing the band gap decreased.

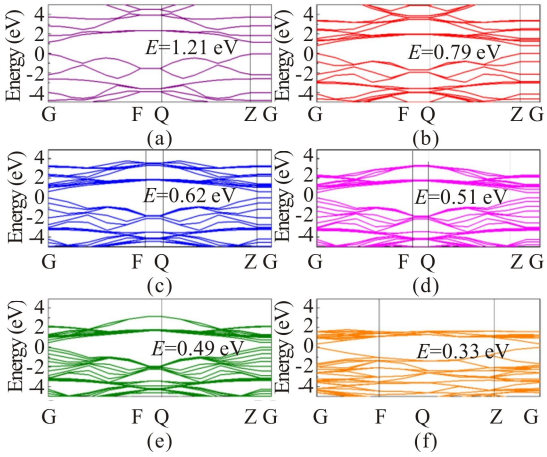


Fig.3 Band structures of black phosphorus with different layers from (a) 1 to (e) 5 and (f) bulk system

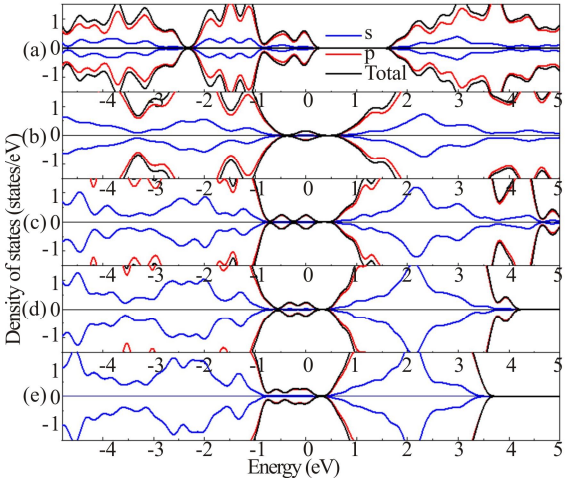


Fig.4 *DOS* of black phosphorus with different layers from 1 to 5

Currently, electronic structures of black phosphorus have been widely investigated in the past year. Thus, it is interesting to reveal the optical transition and optical absorption of black phosphorus.

In the random phase approximation (RPA), local field effects are neglected. In the linear response range, the optical properties of semiconductors are usually described by the dielectric function $\varepsilon(\omega)$, expressed as

$$\varepsilon(\omega)= \varepsilon_1(\omega)+i\varepsilon_2(\omega), \quad (2)$$

where $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are the real and imaginary parts of

the dielectric function, respectively, and ω represents the frequency of electromagnetic waves. The real part of the dielectric function $\varepsilon_1(\omega)$ reflects the transition when the electron releases energy and falls to the lower orbits. The imaginary part of the dielectric function $\varepsilon_2(\omega)$ reflects the absorption of photons by the system, which is calculated by the transition of valence electrons between occupied and unoccupied orbits. Absorption coefficient $\alpha(\omega)$ can be derived from $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ as

$$\alpha(\omega)=\sqrt{2}\omega\left[\sqrt{\varepsilon_1^2(\omega)+\mathrm{j}\varepsilon_2^2(\omega)}-\varepsilon_1(\omega)\right]^{1/2}. \quad (3)$$

We noticed that single layer black phosphorus presented optical transitions of 2.45 eV, which should mainly be caused by the inter-band transition between valence band maximum and conduction band minimum (Fig.5). With the increasing number of layers, the peak of optical transition shifted gradually to the low energy region. The positions of optical transitions were located in 1.97 eV, 1.84 eV, 1.82 eV, 1.80 eV, corresponding to 2, 3, 4, 5 layers, which was consistent with the band gap decreasing from electronic structure calculation as well as previous investigations. In addition, the intensity of transition peak was increased compared to that of single layer, which was due to that multi-layer black phosphorus contain more electronics. DAI et al built three stacked bilayers models, and calculated the imaginary part of frequency dependent dielectric function of different stacked bilayer black phosphorus using HSE06 function, and strong peaks around 1—1.4 eV could be seen. The optical transition position was closer to our result, and the tiny difference was maybe caused by the different calculated methods. Next, we move to the optical absorption spectrum to observe optical properties intuitively.

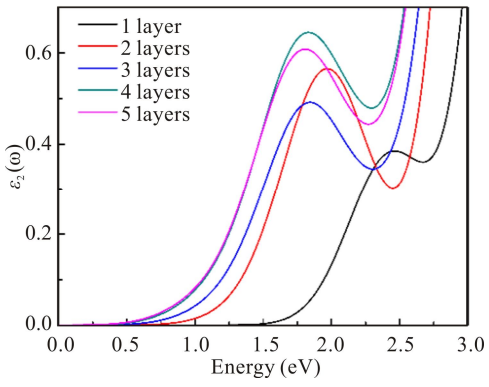
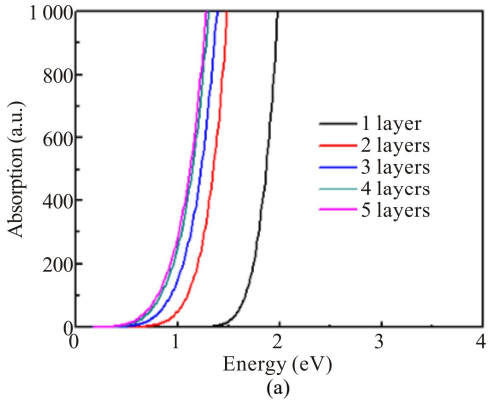


Fig.5 Imaginary part of the dielectric function $\varepsilon_2(\omega)$ of black phosphorus with different layers

Optical absorption is very important for semiconductor, because it can provide some valuable information for optical band gap and can also show important indication to the applications. Fig.6 shows the optical absorption spectra of black phosphorus with different layers. It was observed that the absorption edge of black phosphorus shifted to the low energy range with the increasing number of layers. By using the extrapolation, the optical band gaps of 1.71 eV, 1.20 eV, 1.07 eV, 0.96 eV, and 0.92 eV were obtained, corresponding to 1, 2, 3, 4 and 5 layers, respectively, which was in good agreement with *DOS* result (Fig.2). The optical absorption of few-layer black phosphorus was in the range of 720—1 300 nm, corresponding to 1—5 layers, which was in good agreement with recent experimental data. It is noting that black phosphorus also shows the significant optical absorption in NIR-IIa (1 300—1 400 nm) and NIR-IIb (1 500—1 700 nm) windows. While it was also found that the optical absorption in NIR-II eventually tended to saturate when the number of layers increased to 5, which was due to the very little change of band gap between 4-layer (0.51 eV) and 5-layer (0.49 eV) black phosphorus, for there was no significant difference in electron emission and absorption through interband transitions. Therefore, the NIR-II optical absorption of few-layer black phosphorus can be increased with increasing the layer number to 5, suggesting its potential for NIR-II luminescence. Because NIR-IIa and NIR-IIb can achieve the centimeter penetration depth in tumor and through skull in mice, therefore, these results indicated black phosphorus with proper layer (2—5 layers) is promising for NIR-II emission and biomedical imaging. Since exciton excitation is beyond the scope of this work due to the theoretical and computational scale and precision, the exciton excitation is not reproduced by DFT optical simulation with VASP. The time-dependent density functional theory (TDDFT) simulation with a simplified black phosphorus model is provided in a subfigure (Fig.6) for qualitative explanation. Though the theoretical simulation of excitons is difficult, the absorption peak around 2 500 nm shows the low energy excitation due to the electron-hole binding. Recently, lots of work showed that black phosphorus presented the mid-infrared emission properties and device applications. It can be conceived that black phosphorus will be interesting for band gap engineering and infrared optical properties.

We investigated the electronic structure and NIR-II optical properties of few-layer black phosphorus by the GGA+U method. It was found that band gap of black phosphorus sensitively depended on the number of layers. The band gap of single layer was 1.21 eV, and with



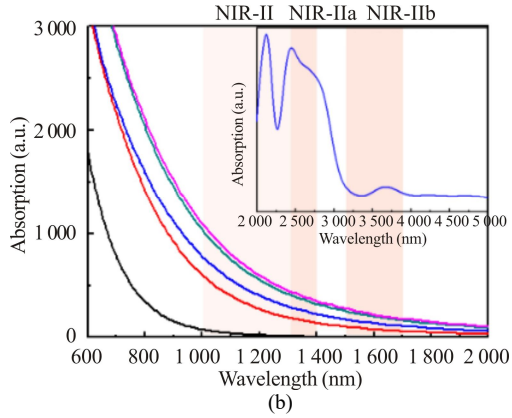


Fig.6 Optical absorption curves of black phosphorus with different layers (The excitonic excitation in sub-figure is simulated by TDDFT): (a) Absorption versus energy; (b) Absorption versus wavelength

the increasing layer number, the band gap decreased to 0.49 eV for 5 layers. Further, the *DOS* confirmed that the increase of p states induced the decrease of band gap when the number of layer was increasing. Finally, we investigated the layer dependent optical absorption and transition of few-layer black phosphorus, and found that optical band edge was shifted to low energy region when increasing the layer, and the wavelength of NIR-II optical absorption was in the range of 720—1 300 nm, corresponding to 1—5 layers. When the number of layers increased to 5, the optical absorption in NIR-II tended to saturate to some extent, suggesting great potential for NIR-II imaging. The layer control of black phosphorus can modulate the band gap and exhibit the NIR-II optical properties.

Statements and Declarations

The authors declare that there are no conflicts of interest related to this article.

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