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The band-edge excitons observed in few-layer NiPS₃Ching-Hwa Ho^{1,2} , Tien-Yao Hsu^{1,2} and Luthviah Choirotul Muhimmah¹

Band-edge excitons of few-layer nickel phosphorous trisulfide (NiPS₃) are characterized via micro-thermal-modulated reflectance (μ TR) measurements from 10 to 300 K. Prominent μ TR features of the A exciton series and B are simultaneously detected near the band edge of NiPS₃. The A exciton series contains two sharp A₁ and A₂ levels and one threshold-energy-related transition (direct gap, E_{∞}), which are simultaneously detected at the lower energy side of NiPS₃. In addition, one broadened B feature is present at the higher energy side of few-layer NiPS₃. The A series excitons may correlate with majorly *d*-to-*d* transition in the Rydberg series with threshold energy of $E_{\infty} \cong 1.511$ eV at 10 K. The binding energy of A₁ is about 36 meV, and the transition energy is $A_1 \cong 1.366$ eV at 300 K. The transition energy of B measured by μ TR is about 1.894 eV at 10 K. The excitonic series A may directly transit from the top of valence band to the conduction band of NiPS₃, while the B feature might originate from the spin-split-off valence band to the conduction band edge. The direct optical gap of NiPS₃ is ~ 1.402 eV at 300 K, which is confirmed by μ TR and transmittance experiments.

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INTRODUCTION

Two-dimensional (2D) semiconductors exhibit immense functionalities and practicalities of large area^{1,2}, ultra-thin^{3,4}, smooth surface⁵, high carrier mobility^{6–8}, flexible layers^{9–11}, and thickness-tunable band-gap modulation^{12,13} that have gradually received blooming attention in semiconductor technological studies and development in the post-silicon era. Among the 2D semiconductors, transition-metal dichalcogenides (TMDCs) MX₂ (M = W, Mo, Re and X = S, Se)^{14–18} comprising a monolayer structure with X–M–X and layered III–VI compounds NX (N = Ga, In and X = S, Se, Te)^{19–23} that are composed of fundamental units of X–N–N–X might be two of the important branches of 2D materials that require further research and development in electronics and optoelectronics devices applications. The TMDC of ReSe₂ has been proven to be a bipolar channel material for application in analog and digital integrated circuits²⁴. The layered TMDCs of WSe₂ and Cr-doped WSe₂ possess the flexibility on bandgap tuning and also stacking phase change from 2H to 1T with the increase of the chromium content²⁵. A plasma-treated MoS₂ device was proposed to be a multibits memory that applied for improving computation speed and data storage capacity²⁶. Conversely, considering III–VI compounds, InSe has been demonstrated as a high-mobility 2D semiconductor (1006–3700 cm²/V-s) that is suitable for the fabrication of high-speed field-effect transistors (FETs)^{7,8}. The native oxidation layer of InO_x on an InSe layer could also produce artificial synapse functions in an InSe FET device²⁷. The layered III–VI GaSe_{1–x}S_x (0 ≤ *x* ≤ 1) series compounds are optically sensitive and can be applied in photodetectors and light-emission devices in the visible-to-ultraviolet region^{28–30}. Recently, as an additional class of 2D layered materials with a monolayer structure between that of TMDCs and III–VI compounds, metal phosphorus trichalcogenides (also known as metal phosphotrichalcogenides) M₂P₂X₆ (M = V, Mn, Fe, Co, Ni, Cd, Mg, or Zn; X = S or Se) have attracted considerable attentions^{31,32}. In the metal phosphotrichalcogenides M₂P₂X₆, each P₂X₆ unit has the valency of 4– [i.e., (P₂X₆)^{4–}]. It is necessary to have M₂⁴⁺ ions for achieving the whole M₂P₂X₆ structure, e.g., Mg₂P₂S₆, Zn₂P₂Se₆, and Ni₂P₂S₆, etc.³¹.

However, the M₂⁴⁺ ions are not usually the same metal elements, thus some of the compounds like CuInP₂S₆, CuCrP₂S₆, and AgInP₂Se₆, etc. also belong to the metal phosphotrichalcogenide family³². According to theoretical and experimental results, the bandgap values of M₂P₂X₆ (as well as MPS₃) range from 1.2 to 3.4 eV³², which may considerably enhance the absorption efficiency and wavelength absorption region compared with those of layered TMDCs having bandgap values of 1.2 to 2 eV. These materials typically own chemical bonding that is intermediate between covalent and ionic as well as exhibit unusual behavior of intercalation–substitution ions, which can render them suitable for applications in Li-ion batteries³³. Moreover, some of the metal elements in this family are usually magnetic (e.g., M = Fe, Ni, Mn and Co). As these metal ions are formed in the van der Waals sheet of M₂P₂S₆, each metal atom would have three equal-distance M neighbors and exhibit stable magnetic phases in the hexagonal lattice. Therefore, layered MPX₃ has been proposed to exhibit specific applications in magneto-optics³⁴, magnetic storage, and 2D magnetism³⁵. The Néel temperature (*T*_N) is an index of the magnetic transition from antiferromagnetic to paramagnetic. The values of *T*_N are ~ 78 K for MnPS₃, ~ 123 K for FePS₃, and ~ 155 K for layered NiPS₃. NiPS₃ exhibits the highest Néel temperature, and the magnetization axis of the ordered states lies along the van der Waals plane, which differs from those of layered MnPS₃ and FePS₃ with out-of-plane axial magnetization³⁵.

Beyond the study of magnetic properties, few-layer semiconducting NiPS₃ also has been fabricated as an ultraviolet photoconductive photodetector with a high detectivity of 1.22×10^{12} Jones as determined via Jones testing with a 254-nm laser³⁶. The heteroatom doping of carbon on the NiPS₃ surface activates the photocatalytic activity of the basal plane and enhances the hydrogen evolution efficiency in the KOH solution³⁷. The catalytic behavior of NiPS₃ also can be exploited to perform water splitting³⁸. A resistive-type humidity sensor with a high sensing speed constructed using layered NiPS₃ also has been proposed³⁹, and an n-channel NiPS₃ FET with an on/off ratio reaching 10³ to

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10^5 also has been reported⁴⁰. Although a few application studies of layered semiconducting NiPS_3 have been reported, the fundamental band-edge nature and optical properties of the nickel phosphotrichalcogenide are not well understood. This in turn limits the development of electronic and optoelectronic devices prepared using NiPS_3 . Some studies have claimed that the bandgap of NiPS_3 is 1.6 eV^{31,32,41}; however, the experimental band-edge structure and excitonic transitions in layered NiPS_3 have not been explored in detail.

In this paper, the band-edge excitons of few-layer NiPS_3 are first observed by temperature-dependent microthermal-modulated reflectance (μTR) measurements in the temperature range between 10 and 300 K. Owing to the reduced dimensionality serving to weaken the dielectric screening effect of electron–hole pairs, 2D materials usually have strong Coulombic interactions in excitons and trions, among others, to form a many-body system, thereby achieving increased excitonic (trionic) binding energy in the layer plane⁴². Excitonic transitions are thus frequently constructed and exist in 2D layered semiconductors. The most renowned cases of this include the A and B excitons that are present in layered MoS_2 ¹², which are also clearly present in the entire series of $\text{Mo}_{1-x}\text{W}_x\text{S}_2$ ($0 \leq x \leq 1$) layers with an energy blue-shift behavior with the increase in the W content⁴³. Another typical case is the five dipole excitons of E_1^{ex} , E_2^{ex} , E_3^{ex} , E_{51}^{ex} , and E_{52}^{ex} , respectively, with a mutual orthogonality of polarization in the layered 2D TMDCs of ReS_2 and ReSe_2 ^{44–46}. In this study, prominent and clear excitonic transitions of few-layer NiPS_3 ($t = 15 \pm 5$ nm) are observed by μTR measurements at 10 K near the band edge. The band-edge excitons of NiPS_3 contain three excitonic features denoted as A_1 , A_2 , and E_∞ in the A series excitons, respectively, while a broadened feature correlates with the band-to-band feature of B. The A_1 , A_2 , and E_∞ μTR features display the Rydberg-series-like transitions with the first level at A_1 , the second level at A_2 , and the continuum band at E_∞ , respectively. The B μTR feature may originate from valence-band (E_v) splitting to the direct conduction-band (E_c) edge transition. The temperature dependences of the energies and broadening parameters of the A series and B obtained via μTR measurements of few-layer NiPS_3 also are analyzed. In addition, temperature-dependent transmittance (optical absorption) measurements of layered NiPS_3 are conducted to verify and identify the absorption edge and excitonic transitions of the A series from 10 to 300 K. The direct optical gap E_∞ of NiPS_3 is determined to be around 1.402 eV at 300 K. According to thickness-dependent micro-photoluminescence (μPL) measurements, an indirect-like E_{3d} emission peak that merged with A_1 is detected at ~ 1.23 eV, while a direct emission of B band also appears at ~ 1.825 eV at 300 K (i.e., $t = 10$ –200 nm). With changing the layer thickness of NiPS_3 , the PL intensities of the E_{3d} emission are also changed, while the intensity of the B-band emission is unchanged from $t = 10$ –200 nm. The Ni 3d e_g^* band may be located intermediate between E_c of $\text{S } 3p^* + \text{P } 3p^* + \text{Ni } 3d^*$ and E_v of $\text{Ni } 3d + \text{S } 3p + \text{P } 3p$ to result in the E_{3d} indirect-like emission in the layered NiPS_3 .

RESULTS

Crystal information and structure

Layered single crystals of nickel phosphotrisulfide NiPS_3 were grown by the chemical vapor transport (CVT) method using I_2 as the transport agent. Supplementary Fig. 1a in the supplementary information (SI) shows the crystal morphology of the as-grown NiPS_3 layered crystals for illustration. The outline of the layered NiPS_3 single crystals essentially reveals a hexagonal shape, and the powdered X-ray diffraction (XRD) pattern shown in Supplementary Fig. 1b exhibits a monoclinic structure (symmetry $C2/m$), with calculated lattice constants of $a = 5.761$, $b = 10.06$, $c = 6.576$ Å, and $\beta = 107^\circ$. These values are in agreement with results obtained

previously for NiPS_3 ^{32,47,48}. Supplementary Figs. 2–4 in the SI also include content analysis conducted by energy-dispersive X-ray analysis and structural characterization using Raman spectroscopy for comparison (see Supplementary Notes 1–2).

The A-series excitons and B band transition in NiPS_3 at 10 K

Figure 1a shows the low-temperature μTR spectrum of a few-layer NiPS_3 sample (i.e., black solid line) measured at 10 K. The upper inset shows a microscope image of the few-layer NiPS_3 nanoflake exfoliated on a SiO_2/Si substrate for the μTR experiment, while the lower inset shows the thickness information determined by atomic force microscopy (AFM). The thickness is about 23 monolayers ($t = 15 \pm 5$ nm) of the layered NiPS_3 crystal. As shown in Fig. 1a, the black solid line is the experimental spectrum, and the green-dashed curve is the least-square fit to a first-derivative Lorentzian line-shape function appropriate for the excitonic transitions expressed as follows⁴⁹:

$$\frac{\Delta R}{R} = \text{Re} \left[\sum_{i=1}^n A_i^{\text{ex}} e^{-j\phi_i^{\text{ex}}} (E - E_i^{\text{ex}} + j\Gamma_i^{\text{ex}})^{-2} \right], \quad (1)$$

where i is the respective transition; A_i^{ex} and ϕ_i^{ex} are the amplitude and phase of the line shape; and E_i^{ex} and Γ_i^{ex} are the energy and broadening parameter of the interband transitions, respectively. As analyzed by the Lorentzian line-shape fitting using Eq. (1), the energy values of two prominent excitonic features (i.e., $A_1 = 1.475$ eV and $A_2 = 1.495$ eV) together with one higher-energy transition (i.e., E_∞ at 1.511 eV) are clearly detected in the A series of few-layer NiPS_3 by μTR . One broadened μTR feature (denoted as B at ~ 1.894 eV) is also found at the higher-energy side of NiPS_3 at 10 K. The transition amplitudes A_i^{ex} of the A series excitons gradually decrease from the maximum $n = 1$ level, progressing to the subsequent $n = 2$ transition, and finally the E_∞ feature follows the general transition probability of the exciton sequence in semiconductors. Modulated TR measurements of semiconductors have been proven to be effective for the characterization of excitons, direct band edge, and interband transitions in the semiconductor's band structure^{50–52}. The derivative spectral line features suppress the unintentional spectral background and emphasize the direct critical-point transitions in the band structure⁵². The TR modulation spectroscopy can be regarded as a physical derivative approach to the reflectance spectrum of semiconductor dielectric function by directly applying thermal perturbation to the crystal lattice periodically (i.e., ΔR). The well-derivative ΔR signal (AC) of sample is thus measured and normalized to the sample reflectance R (DC) for obtaining $\Delta R/R$ at each wavelength using lock-in amplifier. The TR modulation spectroscopy is different from that of reflectance contrast method with firstly measuring $\Delta R/R = (R_{\text{sample}} - R_{\text{substrate}})/R_{\text{substrate}}$ ^{53,54} and then implementing mathematical derivative to the line shape using $(d/dE) (\Delta R/R)$ ⁵³. The μTR technique is directly response to the physical derivative nature of direct transitions in the band structure of the few-layer sample, and thus possesses less substrate effect coming from the SiO_2/Si substrate. Supplementary Fig. 5 shows the bulk TR results of NiPS_3 without any substrate. Essentially the results measured by μTR (with substrate) and measured by conventional TR (without substrate) are similar (Supplementary Note 3). As shown in Fig. 1a, the sharp features of the A series excitons and the extremely broadened B transition reveal that the A and B excitons exhibit different origins in NiPS_3 . The crystal structure of NiPS_3 can be realized as a stacking structure of one-layer trigonal (1T) phase TMDCs such as TiS_2 . Figure 1b shows the atomic arrangements of the side (upper parts) and top (lower part) views of the layered NiPS_3 structure. As the 1T- TiS_2 stacking formula, the NiPS_3 phase is taken as the layered MS_2 (as TMDCs) with the Ti atom replaced by Ni, while 1/3 of the Ni atoms are substituted by the P–P pairs (P_2 dimers) to form $\text{P}_2\text{S}_2 + \text{NiS}_2 + \text{NiS}_2 = \text{Ni}_2\text{P}_2\text{S}_6$ structures that connect and

Fig. 1 Low-temperature excitonic series observed in NiPS_3 . **a** Band-edge excitons of the A series and B transition in few-layer NiPS_3 observed via μTR measurements at 10 K. Insets show the microscopic image and AFM results of the few-layer sample on an SiO_2/Si substrate. The lower inset depicts the representative scheme of Rydberg series absorption for contrast. **b** Atomic arrangements of the side and top views for the layered $\text{Ni}_2\text{P}_2\text{S}_6$ structure. **c** Representative band-edge scheme for the A series exciton and B transition in NiPS_3 .

extend to the entire lamella sheet (monolayer). This situation is clearly demonstrated in the side view of the monolayer NiPS_3 that is displayed in the upper parts of Fig. 1b. Considering the bonding structure of NiPS_3 , the P–P pairs are covalently bonded to six sulfur atoms, and each P atom is tetrahedrally coordinated with three S atoms to form opposite triangles, as shown by the 1T phase shown in the top view of Fig. 1b. Therefore, a $(\text{P}_2\text{S}_6)^{4-}$ fundamental unit exists, and it requires two Ni^{2+} to construct the complete $\text{Ni}_2\text{P}_2\text{S}_6$ layer compound. Because the P_2S_2 is occupied in the 1/3 lattice of layered $\text{Ni}_2\text{P}_2\text{S}_6$, the perfect hexagonal 1T phase is thereby transformed into a monoclinic layered structure of $C2/m$ symmetry. The P_2 dimers also may contribute to the band-edge electronic states of layered NiPS_3 . Therefore, the antibonding states of $\text{S } 3p^* + \text{P } 3p^* + \text{Ni } 3d^*$ may consist in conduction band while the valence band is composed by hybridization of $\text{Ni } 3d + \text{S } 3p + \text{P } 3p$ bonding states. Excepting the incorporation of the P–P pairs, the band-edge contributions of electronic states in E_c and E_v of NiPS_3 can also refer to the TMDCs as MoS_2^{55} , where the largely $\text{Mo } 4d^*$ and minor $\text{S } 3p^*$ are simultaneously consisted in the E_c bottom while major $\text{Mo } 4d$ and $\text{S } 3p$ are positioned at the top of E_v . For the spin–orbit splitting band Δ_{so} , the band contributions may consisted of 60% $\text{Mo } 4d_z^2$ and 40% $\text{S } 3p_z^{55}$. The main difference between the band-edge structures of MoS_2 and NiPS_3 is maybe the magnetic structure of $\text{Ni } 3d$ states that contributed to the antiferromagnet layered NiPS_3 .

According to the analysis of exciton series A observed in Fig. 1a, a modified hydrogen Rydberg model of 2D⁵³ derived from 3D case⁵⁶ may be used to analyze optical transitions and to evaluate binding energy of the observed excitons. In the 2D case, the model

employs an effective Hamiltonian $H = -\hbar^2 \cdot \nabla_r^2 / \mu + V_{e-h}(r)$, where $\mu^{-1} = m_e^{-1} + m_h^{-1}$ (μ : reduced mass) and $V_{e-h}(r) = -e^2 / (\epsilon_{\text{eff}} \cdot r)$ is the locally attractive Coulombic interaction between electron and hole. The term ϵ_{eff} is the effective permittivity of the material available for excitons. The 2D model of exciton predicts an excitonic binding energy expressed as follows:

$$E_b^n = \mu \cdot e^4 / \left[2\hbar^2 \cdot \epsilon_{\text{eff}}^2 \cdot (n - 1/2)^2 \right] = E_\infty - E_{A_n}, \quad (2)$$

where n is the principal quantum number, E_∞ is the threshold energy of the excitonic sequence, and E_{A_n} is the transition energy of the exciton level detected by the layered sample. According this 2D model, a typical case for estimating A series excitons in monolayer (1 L) WS_2 is $E_\infty = 2.41 (\pm 0.04)$ eV and binding energy $E_b^1 = 0.32 (\pm 0.04)$ eV. However, for the thick-layer bulk case (>10 L), because the effects caused by 3D hydrogenic Hamiltonian and excitonic Bohr radius, etc. the direct gap reduces to $E_\infty = 2.10$ eV and E_b^1 decreases to 0.05 eV⁵³. For the $n=2$ level, the energy separation between $n=1$ and $n=2$ is increased with the layer thickness decreases when $t \leq 4$ L. The energy splitting of $n=1$ and $n=2$ will remain the same in bulk case in layered WS_2 ($t > 10$ L)⁵⁷. For NiPS_3 , the A series and B transitions are correlated with majorly $\text{Ni } 3d$ states constructed in E_c and E_v^{58-61} . The A series originates from largely d -to- d transitions correlated with the spin orientation in the antiferromagnetic NiPS_3^{58} . As shown in Fig. 1a, the A_1 level is tentatively assigned to be the $n=1$ level, the A_2 exciton is inferred to be the $n=2$ level, and E_∞ feature is correlated with the direct band gap of NiPS_3 . The lower inset below Fig. 1a depicts the representative scheme of the A_1 , A_2 , and continuum band of bulk

NiPS₃ for analog to the detected A series excitons at 10 K. The A₁ exciton of NiPS₃ has also recently been detected by PL measurement to locate between 1.475 and 1.478 eV with the thickness changing from 3 L to 8 L at 10 K⁵⁸. For the bilayer and monolayer NiPS₃, the PL emission of the A₁ exciton is missing to lend evidence that monolayer NiPS₃ is maybe an indirect-like 2D material. The excitonic PL emission of A₁ also showed linearly-polarized light along the crystal's *a* axis⁵⁸. The polarized behavior of the A₁ exciton is different from the A series exciton in the layered MoS₂¹². The A₁ exciton had been assigned as a Zhang-Rice triplet to a Zhang-Rice singlet transition that correlated with the spin directions in the Ni 3*d* states of NiPS₃⁵⁸. Figure 1c shows the representative band scheme of NiPS₃ appropriate for the transitions of the A series and B observed in Fig. 1a by μ TR. The band block array of NiPS₃ is proposed to be the S 3*p** + P 3*p** antibonding states combined with the lower Ni 3*d** band that is positioned at the bottom of E_C, whereas the fully occupied Ni 3*d* (*t*_{2g} + *e*_g) followed by the S 3*p* + P 3*p* bonding state comprises the main E_V⁵⁷. The Ni 3*d* electron state is *d*⁸, which separates into the lower fully-occupied *t*_{2g}⁶ in E_V (i.e., E_V is mainly Ni 3*d* *t*_{2g}⁶ + P 3*p* + S 3*p*) and the higher half-filled *e*_g² band hybridization with E_C (i.e., E_C is major in Ni 3*d** *e*_g² + P 3*p** + S 3*p**), where P 3*p** antibonding

state contributes to the E_C of NiPS₃^{59,60}. Not only the Ni 3*d* state but also the P 3*p* state hybridizes with the S 3*p* orbital still contributing to the band edge of layered NiPS₃⁶¹. As shown in Fig. 1c, the A series excitons of the A₁, A₂, and E_∞ transitions may originate from the top of E_V by Ni 3*d* to the E_C bottom of NiPS₃, while the B feature is inferred to originate from the spin-orbital splitting of E_V to the E_C bottom. The transition of spin-orbital splitting band to E_C is rather flat to obtain a more broadened B feature as compared to the sharp features of the A series excitons in Fig. 1a.

Temperature-dependent microthermal-modulated reflectance spectroscopy of few-layer NiPS₃

Figure 2a, b shows the temperature-dependent μ TR spectra of the few-layer NiPS₃ sample in the temperature range between 10 and 300 K near the band edge. The dashed lines are the experimental spectra, and the solid curves are the least-square fits using Eq. (1). The obtained transition energies E_i^{ex} of A₁, A₂, E_∞, and B transitions from 10 to 300 K are depicted in Fig. 3a and temperature-dependent broadening parameters Γ_i^{ex} of the A₁ and B μ TR features are shown in Fig. 3b, respectively. The obtained transition energies of A₁, A₂, E_∞, and B at 10 K are indicated by arrows in

Fig. 2 Temperature-dependent μ TR spectra of NiPS₃ near band edge. **a** Temperature dependence of the band-edge excitonic transitions of the A series and B observed in few-layer NiPS₃ via μ TR measurements. The solid lines are the least-square fits of the experimental data to a derivative of the Lorentzian line-shape function in Eq. (1). **b** Magnification of the B transition feature in **a**. **c** 2D contour plot of the μ TR spectra of the A series excitons from 10 to 300 K to illustrate the temperature-energy shift and intensity change. **d** Representative scheme of the experimental setup for the temperature-dependent μ TR measurements.

Fig. 3 Temperature dependence energies and broadening parameters of the A series and B features obtained by μ TR. **a** Temperature-dependent transition energies of the A series and B features obtained by μ TR measurements. The symbols are the data points, solid lines are the least-square fits of the Varshni type, and dashed lines are those of the Bose–Einstein fitting. **b** Temperature dependence of the line-width broadening parameter of the A_1 and B features obtained by μ TR experimentation.

Fig. 2a, b. The energy values are $A_1 = 1.475$ eV, $A_2 = 1.495$ eV, $E_\infty = 1.511$ eV, and $B = 1.894$ eV, respectively. As shown in Fig. 2a, with the increase in the temperature from 10 to 300 K in the few-layer NiPS_3 , band-edge excitons of the A series reveal energy reduction and line-shape broadened characteristics. Figure 2b shows the magnification of the μ TR features of the B exciton from 1.6 to 2 eV (blue box in Fig. 2a): Energy reduction and line-shape broadened characteristics are clearly observed from 10 to 300 K. The transition amplitudes A_i^{ex} of the A series and B features in Fig. 2a, b also demonstrate degradation with the increase in the temperature. Figure 2c shows the 2D contour plot of the μ TR spectra of the A series excitons, A_1 , A_2 , and E_∞ from 10 to 300 K. The energy separation of the $n = 1$ and $n = 2$ levels of NiPS_3 is about 20 meV (Fig. 2(a)). The $n = 2$ exciton level is ionized at $T > 175$ K (Fig. 2a, c). The value of the thermal energy kT (where k is the Boltzmann constant) is in agreement with the energy separation of the $n = 2$ level and E_∞ (~ 16 meV) to facilitate the thermal ionization of the A_2 exciton level. The binding energy of the A_1 level obtained from the Rydberg-series analysis of NiPS_3 in Eq. (1) is about 36 meV. Therefore, the A_1 exciton (i.e., $A_1 \cong 1.366$ eV) can be detected in Fig. 2a for the layered NiPS_3 at 300 K. Figure 2d shows the representative scheme for the experimental setup of the μ TR measurement for the few-layer NiPS_3 . A tungsten halogen lamp dispersed by a monochromator provided the monochromatic light, and which was then guided to a CCD-equipped microscope using optical fiber. The detailed descriptions of the experimental setup are stated in “Methods” section.

Temperature-dependent analysis of A series and B in NiPS_3

Figure 3a shows the experimental data points of the transition energies of the temperature-dependent A series ($n = 1$, $n = 2$, and E_∞) and B features in the few-layer NiPS_3 obtained by the analysis of the derivative Lorentzian line-shape fitting using Eq. (1) that was derived from Fig. 2a, b. The solid lines correspond to the

least-square fits to the Varshni empirical relationship:

$$E_i(T) = E_i(0) - a_i \cdot T^2 / (\beta_i + T), \quad (3)$$

where i is the respective transition, $E_i(0)$ is the energy at 0 K, a_i is related to the strength of the electron (exciton)–phonon interaction, and β_i is closely related to the Debye temperature. Table 1 lists the obtained fitting parameters for comparison. More rapid temperature-energy shift of the E_v top than that of the spin–orbital splitting in the NiPS_3 band indicates that the exciton–phonon interaction strength of the A-series are slightly larger than that of the B band transition. According to the energy difference between B and E_∞ in Fig. 3a, the spin–orbital splitting (Δ_{so}) of the few-layer NiPS_3 is about 0.383 eV. This value is greater than that of about 0.19 eV in the energy separation of the A and B excitons in MoS_2 ^{62,63}. The temperature dependence of the band-edge transition energies of few-layer NiPS_3 also can be analyzed using another expression containing the Bose–Einstein occupation factor for phonons:⁶⁴

$$E_i(T) = E_{\text{IB}}(0) - a_{\text{IB}} \cdot \{1 + 2/[\exp(\theta_{\text{IB}}/T) - 1]\}, \quad (4)$$

where a_{IB} represents the strength of the electron (exciton)–phonon interaction, and θ_{IB} corresponds to the averaged phonon temperature. Figure 3a shows the fitted results represented by the red dashed-dotted curves. The obtained values of $E_{\text{IB}}(0)$, a_{IB} , and θ_{IB} also are listed in Table 1 together with the layered compounds MoS_2 , WS_2 , and $\text{Mo}_{0.5}\text{W}_{0.5}\text{S}_2$ ⁴³, while GaAs ⁶⁴ and ZnSe ⁶⁵ are included for comparison. The values of the Varshni parameter a_i and Bose–Einstein type constant a_{IB} of the A series excitons (A_1 , A_2 , and E_∞) in NiPS_3 are greater than those of the layered TMDs MoS_2 , $\text{Mo}_{0.5}\text{W}_{0.5}\text{S}_2$, and WS_2 . The energy difference of the A exciton between 10 and 300 K is about 110 meV in NiPS_3 , which is greater than those of 70–80 meV for MoS_2 , $\text{Mo}_{0.5}\text{W}_{0.5}\text{S}_2$, and WS_2 . The incorporation of the additional P_2 pairs in layered $\text{Ni}_2\text{P}_2\text{S}_6$ is potentially the main reason for causing a more rapid temperature–energy gap shift compared to the other layered TMDs in the environment of a crystal lattice-constant change.

Table 1. Values of the Varshni and Bose–Einstein type fitting parameters that describe the temperature dependences of the excitonic transition energies of the A_1 , A_2 , E_∞ , and B in the few-layer NiPS_3 together with those previously obtained for MoS_2 , WS_2 , $\text{Mo}_{0.5}\text{W}_{0.5}\text{S}_2$, GaAs , and ZnSe .

Materials	Feature	$E_i(0)$ (eV)	α_i (meV/K)	β_i (K)	$E_{iB}(0)$ (eV)	α_{iB} (meV)	θ_{iB} (K)
NiPS_3^a	A_1	1.476 ± 0.002	0.7 ± 0.04	300 ± 50	1.542 ± 0.001	69 ± 11	250 ± 30
	A_2	1.494 ± 0.002	0.61 ± 0.05	300 ± 50	1.559 ± 0.006	63 ± 13	250 ± 30
	E_∞	1.509 ± 0.002	0.68 ± 0.06	300 ± 50	1.575 ± 0.010	70 ± 22	250 ± 30
	B	1.896 ± 0.003	0.42 ± 0.05	300 ± 50	1.941 ± 0.008	48 ± 8	250 ± 30
MoS_2^b	A	1.935 ± 0.005	0.48 ± 0.05	180 ± 50	1.976 ± 0.02	46 ± 15	220 ± 50
	B	2.142 ± 0.005	0.47 ± 0.05	160 ± 50	2.179 ± 0.02	42 ± 8	200 ± 30
$\text{Mo}_{0.5}\text{W}_{0.5}\text{S}_2^b$	A	1.947 ± 0.005	0.47 ± 0.05	190 ± 60	1.986 ± 0.02	43 ± 12	214 ± 40
	B	2.257 ± 0.005	0.49 ± 0.05	75 ± 60	2.293 ± 0.02	39 ± 10	190 ± 33
WS_2^b	A	2.067 ± 0.005	0.47 ± 0.05	210 ± 50	2.102 ± 0.02	37 ± 10	200 ± 40
	B	2.493 ± 0.005	0.55 ± 0.06	200 ± 50	2.534 ± 0.02	45 ± 11	200 ± 35
GaAs^c	E_g^d				1.512 ± 0.005	57 ± 29	240 ± 102
ZnSe^d	E_g^d				2.800 ± 0.005	73 ± 4	260 ± 10

^aPresent work.
^bsee ref. ⁴³.
^csee ref. ⁶⁴.
^dsee ref. ⁶⁵.

Figure 3b plots the analysis of the broadening parameter Γ (half-width at half-maximum (HWHM)) of the representative A_1 and B features in the μTR spectra of few-layer NiPS_3 between 10 and 300 K with representative error bars. The solid lines represent the least-square fitting to a Bose–Einstein-type formula, which is appropriate for the temperature-dependent line-width analysis as follows:^{64,65}

$$\Gamma_i(T) = \Gamma_{i0} + \Gamma_{iLO}/[\exp(\theta_{iLO}/T) - 1], \quad (5)$$

where Γ_{i0} represents the term of the line-shape broadening invoked from the mechanism of crystallinity from impurities, dislocations, electron interactions, and Auger processes, whereas the Γ_{iLO} term is related to the electron (exciton)–longitudinal optical (LO) phonon (Frohlich) interaction. θ_{iLO} is related to the LO phonon temperature. The obtained fitting parameters of the line-shape broadening of the A_1 and B transitions in NiPS_3 are $\Gamma_{i0} = 7 \pm 1$ and 96 ± 10 meV; $\Gamma_{iLO} = 98 \pm 10$ and 1800 ± 800 meV; and $\theta_{iLO} = 280 \pm 20$ and 584 ± 140 K, respectively. The considerably lower value of Γ_{i0} of the A_1 exciton indicates that an extremely high-quality crystal is obtained for layered NiPS_3 . The broadened B feature implies that the spin–orbital-splitting band is rather flat compared to the E_V top (in k space) that exists in the band structure of NiPS_3 . Because linewidth broadening contributes more significantly than the energy shift with the change in the temperature in the NiPS_3 lattice, the θ_{iLO} value is therefore greater than that of θ_{iB} due to the larger averaged phonon temperature.

Transmittance and optical absorption of NiPS_3 near band edge

To further identify the band-edge nature, temperature-dependent transmittance (T) measurement of a bulk NiPS_3 with a thickness of about 10 μm was conducted. Figure 4a, b show the transmittance absorption edge and μTR spectra of the A and B excitons at 10 and 300 K, respectively, together with a mathematical-derivative transmittance (ΔT) spectrum that is included for contrast. The transmittance spectrum of NiPS_3 clearly reveals the presence of the A_1 , A_2 , and E_∞ excitonic features at the absorption edge at 10 K, similar to those detected in the μTR spectrum. In addition, the ΔT spectrum in Fig. 4a reveals the same energy position and line shape of the A_1 , A_2 , and E_∞ features compared with those

detected in the μTR measurement of NiPS_3 at 10 K. At 300 K, the A_2 feature is ionized, and the energy value of A_1 from μTR is about 1.366 eV. The transmittance edge is extremely close to the A_1 transition, and the ΔT spectral line shape is also similar to that of the μTR feature. These results indicate that the energies of transmittance absorption edge (measured by T) and direct band edge (measured by μTR) of bulk NiPS_3 are very close. This result is dissimilar to other TMDCs such as MoS_2 , whose transmittance absorption edge is at 1.23–1.28 eV (i.e., optical transition assisted by emission and absorption of phonons), while the direct gap is about 1.88 eV in multilayer MoS_2 ⁶⁶. The energy difference between the indirect and direct bandgaps of MoS_2 is about 0.6 eV. The weakened layer-by-layer decoupling of layered NiPS_3 compared to MoS_2 may be the main reason for the small energy difference between the indirect and direct bandgaps of the layered compound. Figure 4c, d show the temperature-dependent transmittance and absorption spectra of the NiPS_3 sample from 10 to 300 K. The absorption spectrum of NiPS_3 at 10 K in Fig. 4d is also similar to previous absorption curve that detected by antiferromagnet NiPS_3 ⁵⁸. The absorption edge in the temperature-dependent transmittance and absorption spectra demonstrates an energy blue-shift behavior with the decrease in the temperature from 300 to 10 K, similar to the typical trend for semiconductors. The clear A_1 , A_2 , and E_∞ transition features of the A series excitons are still observed in the low-temperature absorption spectra ($T < 180$ K), verifying the μTR results of few-layer NiPS_3 in Fig. 2a. At 300 K, a shoulder peak of $E_\infty \approx 1.402$ eV is still observed for NiPS_3 in Fig. 4d. This value is in good agreement with the direct band gap of the layered NiPS_3 obtained using the Rydberg series as $E_\infty \approx A_1$ (1.366 eV) + E_b (36 meV) at room temperature.

Micro-photoluminescence result

To evaluate the origin of the band edge, thickness-dependent micro-photoluminescence (μPL) measurements of layered NiPS_3 were conducted at 300 K. Figure 5a shows the μPL spectrum of a few-layer NiPS_3 sample with a thickness of about 10 nm. Two broadened peaks at about $E_{3d} \approx 1.23$ eV and at $B \approx 1.825$ eV are observed in the μPL spectrum of few-layer NiPS_3 . The E_{3d} peak is strong, but it gradually decreases with the increase of thickness in

Fig. 4 The comparison of transmittance and μTR spectra in NiPS₃. Spectral comparison of the band-edge transitions in the transmittance (T), first-derivative transmittance (ΔT), and μTR spectra at **a** 10 K and **b** 300 K. The temperature-dependent transmittance and absorption spectra of the layered NiPS₃ sample from 10 to 300 K are shown in **c** and **d**, respectively.

layered NiPS₃ (Fig. 5b), whereas the B emission peak remains at a similar PL intensity with the change in the layer thickness from 10 to 200 nm. A detailed analysis of the PL line-shape fitting of the PL spectrum in Fig. 5a reveals that the A₁ peak (at 1.366 eV) is still involved in the broadened E_{3d} peak. The variation of PL intensity of the E_{3d} peak with changing the thickness of NiPS₃ implies that multilayer NiPS₃ is maybe an indirect semiconductor with an indirect-like emission of ~ 1.23 eV, originating from the Ni 3d e_g* band to the E_v transition assisted by phonons at 300 K. The indirect-like emission of a 1.3–1.4 eV peak from indirect E_c valley at Σ point was usually observed in the multilayered MoS₂ (10–200 nm) on SiO₂/Si and on Cu substrate⁶⁷. In the light-emission process, phonons are required to conserve the

momentum, and photoexcited hot electrons are injection into the lower indirect valley of E_c for resulting in indirect-like emission. As shown in Fig. 4b, the transmittance absorption edge of layered NiPS₃ reveals that photons almost pass through at 1.23 eV, while this value starts to decrease until the photon energy becomes 1.366 eV (A₁) at 300 K. This result implies that the Ni 3d e_g* states might form an intermediate band located between the main E_c (P 3p* + S 3p* + Ni 3d*) and the top of E_v. The lower indirect-like emission bands of the M d to d transitions of M₂P₂S₆ also can be observed in previous study of Cd₂P₂S₆⁶⁸. The inset of Fig. 5a shows the probable band scheme of the band edge for PL band-edge emissions. The E_{3d} peak is an indirect-like emission caused by the intermediate band of Ni 3d e_g* existed in NiPS₃. The A₁ and B

Fig. 5 Thickness-dependent μ PL result of few-layer NiPS_3 at 300 K. **a** μ PL spectrum of the band-edge emissions of a few-layer NiPS_3 sample with a thickness of ~ 10 nm at 300 K. The fitting curves of the PL peaks are also included. The left inset shows a microscopic image of the few-layer sample, and the right inset shows the possible band-edge scheme for the observed PL emissions. **b** Thickness dependence of the PL intensities of the E_{3d} and B peaks detected in **a**.

emissions are originated from the direct E_C bottom to the E_V top and to the spin-split-off band below E_V , respectively.

DISCUSSION

In conclusion, the band-edge excitons of A series and B transition were clearly detected and observed in the high-quality few-layer NiPS_3 grown by chemical vapor transport. The prominent excitonic sequence of A_1 , A_2 , and E_∞ transitions and one band-to-band feature of B in NiPS_3 were detected by micro-TR at 10 K. The energy values and amplitudes of the excitonic sequence A_1 , A_2 , and E_∞ followed a Rydberg series and continuum band. The excitonic binding energy of the A_1 level is about 36 meV and its transition energy is 1.366 eV at 300 K. The temperature-dependent μ TR measurements of the A series and B transitions of the few-layer NiPS_3 were conducted to verify the thermal ionization energy of the excitons and the temperature-energy shift of the 2D material from 10 to 300 K. The energy separation of the A_1 , A_2 , and E_∞ transitions was in good agreement with the corresponding ionization temperatures to sustain the detected A series excitons in NiPS_3 . In addition, band-edge excitons of the A_1 , A_2 , and E_∞ transitions were detected in the temperature-dependent transmittance and absorption spectra to identify the existence of the A series excitons in the layered NiPS_3 . The direct optical gap of

few-layer NiPS_3 was determined to be $E_\infty \approx 1.402$ eV at 300 K. The temperature-energy shift of the A series excitons between 10 and 300 K was faster than those of MoS_2 and WS_2 . From the μ PL measurement of few-layer NiPS_3 , the indirect-like emission was observed at 1.23 eV, while a direct B band emission was observed at 1.825 eV. The indirect-like emission possibly originates from an intermediate band of $\text{Ni } 3d e_g^*$ to the E_V top recombination. The A series excitons come from the top of E_V to the E_C bottom, while the B feature is originated from the spin-split-off band to the E_C transition. Based on the experimental analysis, the origin of the band-edge excitons of the layered nickel phosphorus trisulfide was realized.

METHODS

Sample growth

Test samples were prepared by growing the layered single crystals of NiPS_3 via CVT with I_2 as the transport agent. First, powdered elements of Ni (99.99% purity), P (99.999% purity), and S (99.999% purity) were prepared. Second, the powder mixture of the starting materials and an appropriate amount of I_2 (10 mg/cm³) were cooled with liquid nitrogen and sealed in a vacuum environment at $\sim 10^{-6}$ Torr inside a quartz ampoule. The growth temperature was set as 800 °C (heating zone) $\rightarrow$ 700 °C (growth zone) with a gradient of -2.5 °C/cm for the simultaneous growth in two ampoules. The reaction occurred over 336 h to grow large single crystals. After this growth, several shiny sheet-like NiPS_3 thick crystals with areas up to a scale of square centimeters were obtained. With the weakened van der Waals bonds between the layers, different layer thicknesses of NiPS_3 can be mechanically exfoliated and transferred onto a SiO_2/Si substrate using Scotch tapes with different stickiness properties.

Microthermal-modulated reflectance

For μ TR measurements, a 150-W tungsten halogen lamp served as the white light source. The white light source was dispersed by a 0.2-m Photonics International (PTI) monochromator, which was equipped with a 1200-grooves/mm grating for providing monochromatic light. The SiO_2/Si substrate decorated with few-layer NiPS_3 (size of $0.8 \times 0.8 \times 0.01$ cm³) was closely attached onto an Au-evaporated quartz plate. The monochromatic light source was coupled onto the few-layer or multilayer sample using a silica fiber, and it passed through a light-guiding microscope (LGM) equipped with an Olympus objective lens (50 $\times$, working distance ~ 8 mm). It served as the interconnection coupled medium between the few-layer sample and the incident and reflected lights⁶⁹. The reflected light from the layered sample was collected by the LGM and then coupled to an EG&G HUV200B Si detector using an additional silica fiber. Optical alignment was accomplished by the XYZ adjustment of the nano-flake sample using a CCD imaging camera in the LGM. A 4-Hz heating current (~ 0.5 A) was periodically supplied to the Au heater for the thermal modulation of the lattice constant and band edge of the sample. Phase-sensitive detection was achieved by using an NF 5610B lock-in amplifier. A Janis open-circled liquid-helium cryostat equipped a Lakeshore 335 thermometer controller was used to facilitate temperature-dependent measurements from low temperatures to room temperature.

Optical transmission measurement

For the transmission measurement of bulk NiPS_3 sample, the same monochromatic light source as that employed for μ TR was used. The layer sample of $t \sim 10$ μm was closely mounted on a copper holder with a center hole of size approximately 500 μm for light transmission. The incident light was chopped at 200 Hz with an optical chopper. The transmission light of the sample was passed to an EG&G HUV200B Si photodetector. An NF 5610B lock-in amplifier was used to implement the phase-sensitive photodetection. An RMC 22 close-cycled He compressor system that was equipped with a Lakeshore 335 thermometer controller facilitated the low temperature and temperature-dependent measurements.

Micro-photoluminescence experiment

The μ PL measurements were conducted in an integrated RAMaker microscope spectrometer with a 532-nm solid-state diode-pump laser as the excitation source. The same LGM setup as that used for μ TR was utilized for the interconnection coupled medium between the few-layer

NiPS₃ sample, the incident and reflected (scattered) lights, and the charge-coupled-device (CCD) spectrometer. The laser power was 5 mW, and the laser spot size was 3–5 μm. The measurements were obtained from 1.1 to 2.25 eV.

DATA AVAILABILITY

The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

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AUTHOR CONTRIBUTIONS

C.H.H. conceived the idea and conducted the experiments. T.Y.H. grew the samples and performed the optical measurements. L.C.M. did the micro-PL experiment. C.H.H. also analyzed (calculated) the measurement data, and wrote the manuscript.

COMPETING INTERESTS

The authors declare no competing interests.

ADDITIONAL INFORMATION

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