Extraordinarily bound quasi-one-dimensional trions in two-dimensional phosphorene atomic semiconductors

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We report a trion (charged exciton) binding energy of ~180 meV in few-layer phosphorene at room temperature, which is nearly one to two orders of magnitude larger than those in two-dimensional (2D) transition metal dichalcogenide (TMD) semiconductors (20–30 meV) and quasi-2D quantum wells (~1–5 meV). Such a large binding energy has only been observed in truly one-dimensional (1D) materials such as carbon nanotubes, whose optoelectronic applications have been severely hurdled by their intrinsically small optical cross-sections. Phosphorene offers an elegant way to overcome this hurdle by enabling quasi-1D excitonic and trionic behaviors in a large 2D area, allowing optoelectronic integration. We experimentally validated the quasi-1D nature of excitonic and trionic dynamics in phosphorene by demonstrating completely linearly polarized light emission from excitons and trions in few-layer phosphorene. The implications of the extraordinarily large trion binding energy in a higher-than-one-
dimensional material are far-reaching. It provides a room-temperature 2D platform to observe the fundamental many-body interactions in the quasi-1D region.

A neutral exciton is a bound quasi-particle state between one electron and one hole through a Coulomb interaction, similar to a neutral hydrogen atom. A trion is a charged exciton composed of two electrons and one hole (or two holes and one electron), analogous to H⁻ (or H₂⁺)\(^1\). Trions have been of considerable interest for the fundamental studies of many-body interactions, such as carrier multiplication and Wigner crystallization\(^2\). In contrast to the exciton, a trion has an extra charge with nonzero spin, which can be used for spin manipulation\(^3\). More importantly, the density of trions can be electrically tuned by the gate voltage, enabling remarkable optoelectronic applications\(^1\)\(^-\)\(^5\). For these purposes, a large trion binding energy is critical in order to overcome the room-temperature thermal fluctuations as well as to widen the spectral tuning range. The dimensional confinement is the dominating factor that determines the binding energy of trions. In quasi-2D quantum wells, the trion binding energy is only 1–5 meV, and trions are highly unstable, except at cryogenic temperatures\(^1\)\(^-\)\(^6\). Recently, Shan\(^7\) and Xu\(^8\) made an important breakthrough, showing that truly 2D atomic TMD semiconductors have trion binding energies up to 20–30 meV, which is still barely resolvable at room temperature compared with their emission bandwidth. On the other hand, trions in the 1D space, such as carbon nanotubes, exhibit remarkably higher binding energies in the range of 100–200 meV owing to the stronger Coulomb interaction with the reduced dimensionality and screening\(^9\). The complete separation of the exciton and trion emission peaks was observed at room temperature\(^9\). However, the application of 1D carbon nanotubes for practical optoelectronic devices is intrinsically limited by their small cross-sections. The overall optical responses of such 1D lines are extremely weak. The diverse distribution of the chirality in carbon nanotubes also makes it impossible to assemble a large-size film with uniform optoelectronic responses. While the reduced dimensionality
leads to far more attractive exciton and trion properties, the trade-off between the cross-section and the dimensional confinement has hindered the development of useful excitonic optoelectronic devices.

The anisotropic nature of the new 2D material phosphorene, in contrast to other 2D materials such as graphene and TMD semiconductors, allows excitons to be confined in a quasi-one-dimensional (quasi-1D) space predicted in theory, leading to remarkable phenomena arising from the reduced dimensionality and screening. Here, we show that phosphorene presents an intriguing platform to overcome the aforementioned trade-off. We observed quasi-1D trions with ultra-high binding energies up to ~180 meV in 2D phosphorene atomic semiconductors. Using back-gated metal-oxide-semiconductor (MOS) devices, we demonstrated the reversible electrostatic tunability of the exciton charging effects between trions and excitons in 3L phosphorene. The measured ultra-high trion binding energies (~180 meV), comparable to those in truly 1D semiconductors, are due to the formation of quasi-1D trions and excitons in 2D phosphorene. The quasi-1D excitons and trions in phosphorene were demonstrated by our measured linearly polarized PL emission from the excitons and trions. In this regard, phosphorene is equivalent to a system that is made of a bundle of identical 1D materials. Our results open exciting avenues for optoelectronic applications, including tunable light sources, spin manipulation devices, and quantum logical systems.

This new type of material, few-layer phosphorene, is unstable and does not survive well in many standard nanofabrication processes. To overcome the challenge of the instability, we designed special fabrication and characterization techniques. We used mechanical exfoliation to dryly transfer a phosphorene flake onto a SiO$_2$/Si substrate (275 nm thermal oxide on n$^+$-doped silicon). The phosphorene was placed near a gold electrode that was pre-
patterned on the substrate. Another thick graphite flake was similarly transferred to electrically bridge the phosphorene flake and the gold electrode, forming a MOS device (Figure 1). These two steps can avoid the possible sample cracks if we directly transfer the thin phosphorene flake onto the un-flat edge of the gold electrode. This fabrication procedure kept the phosphorene free from chemical contaminations by minimizing the post-processes after the phosphorene flake was transferred. In the measurement, the gold electrode is grounded, and the n⁺-doped Si substrate functions as a back gate providing uniform electrostatic doping in the phosphorene (Figure 1b). The layer number of the phosphorene sample was precisely identified by phase-shifting interferometry (PSI), which was demonstrated by us to be a very reliable and fast way to determine the layer number for phosphorene samples. After the PSI, the sample was placed into a microscope-compatible chamber for photoluminescence (PL) measurements, with a slow flow of nitrogen gas to prevent the degradation of the sample. The layer number was further confirmed by the measured PL spectra.

Trions, having a many-body bound state, are formed through the interplay between the exciton and carrier. The density of trions can be modulated by controlling the carrier doping level using various methods, such as electrostatic modulation, and chemical doping. Here, we demonstrate the reversible electrostatic tunability of the exciton charging effects from positive (A⁺) to neutral (A°) in a 3L phosphorene MOS device (Figure 2), using gate-dependent PL measurements. The measured PL spectra exhibit two clear peaks with central wavelengths at ~1100 and ~1300 nm, whose intensities are highly dependent on the back-gate voltage. The higher-energy peak (~1100 nm) is attributed to the exciton emission, and the lower-energy peak (~1300 nm) is due to the trion emission. To show the evolution of the exciton and trion, we applied a gate voltage Vg to pump extra charges into the phosphorene. We used Lorentzian curves to fit the measured PL spectra to extract the exciton
and trion spectral components, as indicated by the red and blue curves in Figure 2a, respectively. The Si/SiO$_2$ substrate also has a PL peak at $\sim$1100 nm that is independent of the gate voltages (Figure S1). The emission intensity from the substrate is far weaker than that from phosphorene, and it can be easily separated from the measured voltage-dependent PL spectra (Figure 2a).

At a voltage bias of -50 V, positive charges are pumped into the phosphorene, and almost all excitons become charged trions. As a result, the PL emission from neutral excitons $A^\circ$ at a wavelength of $\sim$1100 nm is absent (Figure 2a). In contrast, the PL emission from positive trions $A^+$ at $\sim$1300 nm is extremely strong. As we gradually depleted the positive charges by changing the voltage from -50 to 50 V, the PL emission from the neutral excitons became increasingly prominent at $\sim$1100 nm, while that of the positive trions became progressively weaker (Figure 2a and 2b) simultaneously. From the measured field effect transistor (Figure S2) $I_{ds}$-$V_g$ characteristics (Figure 2b), we could clearly see that the emergence of the charged exciton peak correlates with the onset of electrostatic doping, which is similar to the modulation of trions in monolayer MoS$_2$. Such a transfer of the spectral weight is directly caused by the depletion of positive charges, i.e., $A^+ - h \rightarrow A^\circ$, where $h$ represents a hole. In principle, negative trions can also be expected when $V_g$ is large enough to introduce sufficient electron doping to offset the intrinsic hole doping in the phosphorene layer, which can be realized by replacing the thick oxide layer with thin, high-$k$ dielectric materials. As shown in Figure 2C, the peak energy difference between excitons and trions decreased from 188 to 170 meV, when the gate voltage increased from -50 to 50 V. The central wavelengths of the emission peaks from $A^\circ$ and $A^+$ are slightly dependent on the back-gate voltages (Figure 2c), which could be due to the change of Fermi level at different biases. The peak energy difference between $A^\circ$ and $A^+$ exhibits a large value of $\sim$180 meV, which is the trion binding energy. Remarkably, such a large binding energy has not been observed in any other
higher-than-one-dimensional material. It is comparable to that from 1D semiconductors\textsuperscript{9,28} and is approximately one order of magnitude larger than that from TMD 2D semiconductors\textsuperscript{14,15}. Positive trions with a large binding energy have been observed in multiple 3L phosphorene MOS devices (Figure S3).

In our experiments, the low-energy emission peak at ~1300 nm have opposite doping dependence with the high-energy emission peak, which agrees well with the unique behaviour of trions\textsuperscript{7}. In order to further confirm the trion assignment for the low-energy PL emission at ~1300 nm, we did excitation power dependent PL measurements (Figure 3a). As shown by Yu \textit{et al.}\textsuperscript{27} and Heinz \textit{et al.}\textsuperscript{29}, the integrated PL intensities of localized excitons, trions/excitons, and bi-excitons, grow sub-linearly, linearly, and quadratically, respectively, with the excitation powers\textsuperscript{27,29,30}. From our measurements, integrated PL of the low-energy peak at ~1300 nm from the 3L phosphorene sample grows linearly with the excitation power ($\alpha = 1.1$, Figure 3a), indicating that the peak at ~1300 nm is indeed from trions, but not from bi-excitons or localized excitons, while the high-energy PL peak (~1100 nm) has been assigned to be from excitons.

Besides the electrostatic doping, substrate-induced doping can also be used to modify the spectral weight between neutral excitons and trions in the PL spectra from 2D semiconductors\textsuperscript{31}. For instance, the trion emission dominates in 1L MoS\textsubscript{2} on SiO\textsubscript{2} substrate, while the neutral exciton emission dominates in 1L MoS\textsubscript{2} on gold substrate, since 1L MoS\textsubscript{2} has an initial n-type doping and the gold substrate can reduce the doping level via charge transfer between the gold-MoS\textsubscript{2} interface\textsuperscript{31}. Although the tunability of the excitons and trions through electrical gate is obvious in Figure 2a, the exciton emission peak at ~1100 nm from 3L phosphorene partially overlaps with the PL emission of the silicon substrate. In order to get rid of the PL influence from silicon substrate and see the exciton emission of 3L...
phosphorene more clearly, we transferred a 3L phosphorene sample onto a gold substrate. Interestingly, the unambiguous exciton emission peak at ~1080 nm was observed from the 3L phosphorene on gold (Figure 3b), in contrast to the dominant trion emission peak at ~1300 nm from 3L phosphorene on SiO$_2$ substrate. This strongly substrate-dependent PL response can be understood from the charge transfer between the 3L phosphorene and the gold substrate, as indicated in the schematic plot of the band diagram$^{32}$ (Figure 3c). During the PL measurements, the excited holes will move towards the gold surface and then annihilate with the electrons from gold, which can significantly reduce the doping level (from the initial p-type dopants) in 3L phosphorene and make the PL emission from neutral excitons to be dominant. This charge transfer can also quench the intensity of the PL emission. That is why the PL intensity from the 3L phosphorene on gold is relatively low, which is similar to that from 1L MoS$_2$ on gold$^{31}$. Owing to the significant reduction of the doping level and the quenching effect, the trion peak at ~1300 nm was not observed from the 3L phosphorene on gold substrate.

The ultra-high trion binding energy measured in few-layer phosphorene is caused by the material’s unique anisotropic quasi-1D excitonic nature, which can be measured using the linearly polarized emission, as theoretically predicted by Yang et al$^{17}$. Here, we demonstrate the quasi-1D nature of the excitons and trions in few-layer phosphorene using PL measurements with an angle-resolved excitation and emission. We show that the PL emissions are completely linearly polarized along the armchair direction of the crystal. In the setup of the angle-resolved PL measurement (Figure 4a), a linearly polarized Nd:YAG laser with a wavelength of 532 nm was used as the excitation source. The polarization angle of the incident light ($\theta_1$) is controlled by an angle-variable half-wave plate. The polarization angle of the emission ($\theta_2$) is characterized by inserting an angle-variable polarizer in front of the detector. $\theta_1$ and $\theta_2$ are relative to the same zero-degree reference, which can be arbitrarily
selected in the beginning. According to the polarization-dependent PL excitation, we can
determine the crystalline orientation of the phosphorene flake, and then the zigzag direction is
selected as the shared zero-degree reference for $\theta_1$ and $\theta_2$ (Figure 4b inset). In the first
characterization of the PL excitation polarization dependence, only the half-wave plate was
used, and the polarizer in front of the detector was removed. We found that the PL intensity
strongly depends on the excitation polarization angle $\theta_1$ (Figure 4b and Figure S4). This
strong PL excitation polarization dependence is due to the highly anisotropic optical
absorption in the phosphorene$^{16, 17}$. Because of the symmetry in its band structure and the
optical selection rules$^{33}$, phosphorene strongly absorbs armchair-polarized light and is
transparent to zigzag-polarized light with energies between 0.5 and 2.8 eV$^{17}$. Next, we
measured the polarization of the PL emission by fixing the excitation polarization angle $\theta_1$.
We observed the maximum PL intensity at $\theta_2 = 90^\circ$ and the minimum PL intensity at $\theta_2 = 0^\circ$
(Figure 4c and 4d). From figure 4c and figure 4d, we could clearly see that the PL emissions
from both trions (~1300 nm) and excitons (~1100 nm) in the 3L phosphorene are completely
linearly polarized along the armchair direction. The measured linear dichroism (LD) values
for the PL emissions are all close to unity in few-layer phosphorene samples (Figure 4c and
4d). LD is defined as $LD = (I_x - I_y)/I_x$, where $I_x$ and $I_y$ are the PL emission peak intensities
along the armchair and zigzag directions, respectively. The polarization of the PL emission is
independent of the excitation and is determined by the intrinsic properties of phosphorene$^{33}$.

To better understand the extraordinary trion binding energy (as large as ~180 meV) for 3L
phosphorene, a theoretical analysis is important. Up to now, exciton and trion binding
energies have been calculated using many different well-developed approaches, such as
diffusion Monte Carlo technique$^{34, 35}$, boundary-matching-matrix method$^{36}$ and
hyperspherical approach$^{37, 38}$, etc. However, they are mainly applicable for 2D TMDs
semiconductors and quasi-2D GaAs quantum wells$^{34-38}$. We tried to implement these
approaches for 3L phosphorene and got the trion binding energy of 50 – 70 meV\textsuperscript{34-38}, which is lower than the value measured from our experiments. This is primarily because the excitons and trions in phosphorene are confined to a quasi-1D space, which has been demonstrated by our angle-resolved PL measurements on 3L phosphorene samples. Here, we calculate the quasi-1D trion binding energy using variational quantum Monte Carlo method, because this approach has been demonstrated to work well for both quasi-1D trions from carbon nanotubes and quasi-2D trions from GaAs quantum wells\textsuperscript{9, 28, 39-41}. The binding energies of excitons ($E_E$) and trions ($E_T$) can be estimated using following equation\textsuperscript{41}:

\[
E_E = \frac{4}{(D_E - 1)^2} \times R_y^* \\
E_T = \left( -\frac{4}{(D_E-1)^2} - c_0 - \sum_{i=1}^{4} c_i D_T^{-i} e^{-D_T} \right) \times R_y^* 
\]

where $D_E$ is the effective dimension of excitons, $D_T$ is the effective dimension of trions, $R_y^*$ is the effective Rydberg and $c_i, i=1-4$ are coefficients\textsuperscript{41} given in Supporting Information Table S1.

The effective dimension of a trion is expected to be slightly smaller than that of an exciton, because of the extra charge in the trion\textsuperscript{41}. For calculation and analysis convenience\textsuperscript{41}, we can simply the equation by taking $D = D_E = D_T$.

\[
E_E = \frac{4}{(D - 1)^2} \times R_y^* \\
E_T = \left( -\frac{4}{(D-1)^2} - c_0 - \sum_{i=1}^{4} c_i D^{-i} e^{-D} \right) \times R_y^* 
\]
The calculated trion binding using this simplified equation (2) is expected to be slightly smaller than that from the original equation (1). Based on this simplified equation (2), we calculated the trion and exciton binding energies as a function of the effective dimension $D$ in 3L phosphorene (Figure S5). Using the measured trion binding energy value of $\sim$180 meV in 3L phosphorene, we can estimate the effective dimension of trions in 3L phosphorene to be $D \sim 1.6$, which further supports the quasi-1D nature of trions demonstrated earlier. Based on previous theoretical calculations, the trion binding energies of TMDs materials are 10%-15% of their exciton binding energies$^{34-38}$, and this has been confirmed by experimental measurements in TMD semiconductors$^{7, 8, 42-44}$. Based on Tran’s simulation$^{17}$, the exciton binding energy of monolayer phosphorene ($\sim$0.9 eV) is higher than the exciton binding energies of all reported TMD monolayers$^{34-38, 42, 43}$, because of the quasi-1D exciton nature in phosphorene$^{17}$. More importantly, based on Equation 2 and Figure S5, the binding energies of excitons and trions increase with the decrease of the effective dimensionality of the excitons and trions in the materials. And this is the main reason that trions in the 1D space, such as carbon nanotubes, own remarkably higher binding energies in the range of $\sim$200 meV$^9$.

In conclusion, we observed extraordinarily bound quasi-1D trions in 2D phosphorene atomic semiconductor crystals. The measured ultra-high trion binding energies in few-layer phosphorene are approximately one order of magnitude higher than those in 2D TMD semiconductors. The large trion binding energy is due to the strongly confined quasi-1D excitonic nature in few-layer phosphorene, which is demonstrated by our measured linearly polarized PL emission. Phosphorene possesses both a large optical cross-section, as typically exhibited by a 2D material system, and high trion binding energies, as typically exhibited by a 1D system, allowing remarkable optoelectronic applications, including tunable light sources, photo-detectors and spin manipulation devices. Few-layer phosphorene also serves as a room-temperature platform for investigating many-body interactions and excitonic physics.
Methods

Device Fabrication and Characterization. We used mechanical exfoliation to drily transfer a phosphorene flake onto a SiO₂/Si substrate (275 nm thermal oxide on n⁺-doped silicon), near a pre-patterned gold electrode. The gold electrodes were patterned by conventional photolithography, metal deposition, and lift-off processes. Another thick graphite flake was similarly transferred to electrically bridge the phosphorene flake and the gold electrode, forming a MOS device. All PL and polarization measurements were conducted using a T64000 micro-Raman system equipped with a charge-coupled device (CCD) and InGaAs detectors, along with a 532nm Nd:YAG laser as the excitation source. Subsequent to PSI measurement, the sample was placed into a Linkam THMS 600 chamber, with a slow flow of nitrogen gas to prevent degradation of the sample. To avoid laser-induced sample damage, all PL spectra were recorded at low power levels: P ~ 20 μW. For the PL measurements, an integration time of 30 seconds was used. The electrical bias was applied using a Keithley 4200 semiconductor analyzer.

Numerical Simulation. Stanford Stratified Structure Solver (S4) was used to calculate the phase delay. The method numerically solves Maxwell’s equations in multiple layers of structured materials by expanding the field in the Fourier-space.

Author Contributions

Y. R. L. designed the project; S. Z. did the PL and Raman measurements and data analysis; R. J. X. conducted the device fabrication, PL data fitting analysis, and part of the theoretical calculations; S. Z. and R. J. X. conducted the PSI measurements; J. Y., J. J. P., and Y. W. M. contributed to sample preparation; B. B. X. performed the image post-processing; F. W. and
L. F. built the optical characterization setup; Z. W. and Z. F. Y performed the theoretical simulations for the OPL of phosphorene. All authors contributed to the manuscript.

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Competing Financial Interests

The authors declare that they have no competing financial interests.
References


FIGURE CAPTIONS

Figure 1 | Phosphorene characteristics and devices. a, Schematic plot of phosphorene layer structure. b, Schematic plot of a phosphorene MOS device. c, Optical microscope image of the MOS device with Tri-layer phosphorene (labeled as “3L”). d, Phase shifting interferometry (PSI) image of the region inside the box indicated by the dashed line in (c). e, PSI measured OPL values versus position for 3L phosphorene along the dashed line in (d). Inset: schematic plot indicating the PSI measured phase shifts of the reflected light from the phosphorene flake ($\phi_{BP}$) and the SiO$_2$ substrate ($\phi_{SiO_2}$). The OPL is determined as $OPL_{BP} = -\frac{\lambda}{2\pi} (\phi_{BP} - \phi_{SiO_2})$, where $\lambda = 535$ nm is the wavelength of the light source$^{45}$.

Figure 2 | Gate dependence of the exciton and trion in a 3L phosphorene MOS device. a, Measured photoluminescence (PL) spectra (solid dark grey lines) under various back-gate voltages. PL spectra are fit to Lorentzians (solid red lines are the exciton components, solid blue lines are the trion components, solid light grey lines are the Si components, and dashed pink lines are the cumulative results for the fitting). b, PL intensity of exciton and trion (left), drain-source current as a function of gate voltages. The emergence of the charged exciton peak correlates with the onset of electrostatic doping. c, Peak energy of exciton and trion as a function of gate voltage. d, schematic plot showing the dissociation of a trion into an exciton and a hole at the Fermi level.

Figure 3 | Power dependence of trion emission and substrate-induced PL modification in a 3L phosphorene. a, Measured integrated PL intensity of the trion emission (~1300 nm), from a 3L phosphorene sample on a SiO$_2$/Si substrate, as function of the applied laser power. The dashed line represents the power-law fit, with exponent of $\alpha = 1.1$. b, Measured PL spectra from a 3L phosphorene on gold substrate and PL spectra from the gold substrate as background comparison. And the gold substrate is not grounded during the experiment. c,
Schematic plot of the energy band diagram for the 3L phosphorene-gold hybrid system, showing the charge transfer and the quenching effect during the PL process.

**Figure 4 | Quasi-1D trions and excitons in 3L phosphorene.** a, Schematic plot of setup for measurement to characterize the polarization dependence of PL excitation and emission. The polarization angle ($\theta_1$) incident excitation light is controlled by an angle-variable half-wave plate, and the polarization angle ($\theta_2$) of the PL emission is characterized by inserting an angle-variable polarizer in front of the detector. b, Measured excitation polarization dependence of the trion emission (~1300 nm) peak intensities from a 3L phosphorene on SiO$_2$/Si substrate. For this measurement, the polarizer in front of the detector was removed. Inset: schematic plot showing top view of phosphorene lattice structure and coordinates for polarization angles $\theta_1$ and $\theta_2$. c-d, Measured polarization dependence of the trion ($A^+$) emission at ~1300 nm (c) and the exciton ($A^0$) emission at ~1100 nm (d), measured from a 3L phosphorene on SiO$_2$/Si, with a fixed excitation angle of 95°.
Figure 1

(a) Phosphorene 3L
(b) Graphite
(c) Substrate
(d) Optical path length (nm)
(e) Scan distance (μm)
Figure 2
Figure 3

(a) Experiment results and linear fit. Integrated PL (a.u.) vs. Laser power (µW) with an exponent of $\alpha \approx 1.1$.

(b) PL intensity (counts) vs. Wavelength (nm) for Phosphorene 3L and Au with fitted curve.

(c) Energy level diagram showing $E_c$, $E_F$, and $E_v$ with an Au region.
Figure 4

(a) zeigt eine schematische Darstellung der verwendeten Geräte und Prozesse.

(b) zeigt ein Diagramm zur Excitationspolarisation $\theta_1$ (Grad).

(c) zeigt ein Diagramm für die Trion-A-Species $A^+$, mit einem Maximalwert bei etwa 1300 nm.

(d) zeigt ein Diagramm für die Exciton-A-Species $A^0$, mit einem Maximalwert bei etwa 1100 nm.
Supplementary Information for

Extraordinarily bound quasi-one-dimensional trions in two-dimensional phosphorene atomic semiconductors

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1. Photoluminescence (PL) measurements from multiple 3L phosphorene devices

![Figure S1](attachment:figure_s1.png)

**Figure S1 | Photoluminescence (PL) from the SiO₂/Si substrate used for the MOS device under different back-gate voltages.** PL spectrum of the 3L phosphorene MOS at gate voltage of 50 V (shown in Figure 2a) is also plotted here for comparison. Insert: Schematic of the measurement positions. The PL measurement conditions are kept the same for the phosphorene sample and the SiO₂/Si substrate.

In Figure S1, the PL spectra measured from the SiO₂/Si substrate at back-gate voltages of -50, 0 and 50 V are almost identical, originating from the voltage independent Si PL at ~1100 nm; whereas the PL peak intensity at ~1100 nm from the 3L phosphorene MOS device under back-gate voltage 50 V is even higher than that from the substrate. Based on this, we believe that the ~1100 nm PL peak on 3L phosphorene comes from both the phosphorene and Si substrate. The emission intensity from the substrate is much weaker than that from phosphorene and it can be easily separated from the measured voltage-dependent PL spectra (Figure 2a).
Figure S2 | Optical microscope image (a) and schematic (b) of device structure of a few layer phosphorene field effect transistor.

Figure S3 | Gate dependence of the exciton and trion in another 3L phosphorene MOS device. The Si PL spectrum measured from the substrate of this device is also shown for comparison. Note that the Si PL peak intensity here is slightly different from the one shown in Figure S1, due to a slight difference of the laser excitation power used in these two measurements.
Figure S4 | PL spectra from a 3L phosphorene sample at different excitation polarization angle (20°, 50° and 80°).

Because of the band symmetry and the optical selection rules in phosphorene\(^1\), phosphorene strongly absorbs armchair-polarized light and is also transparent to zigzag-polarized light. However, the band gap of phosphorene is not sensitive to polarization angle. Therefore, there is no PL peak shift with the change of polarization angle, which has been confirmed by both reported simulations\(^2\) and our experimental results.
2. Trion binding energy calculation

Table S1. Parameters used for the calculation of trion binding energy in 3L phosphorene.

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<tr>
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where $\mu$ is reduced mass and $\varepsilon$ is dielectric constant.

Figure S5 | Calculated trion and exciton binding energy as a function of effective dimension in 3L phosphorene.
Reference


