Highly Enhanced Many-Body Interactions in Anisotropic 2D Semiconductors

Ankur Sharma,† Han Yan,† Linglong Zhang,‡‡ Xueqian Sun,‡ Boqing Liu,† and Yuerui Lu*,†

†Research School of Engineering, College of Engineering and Computer Science, The Australian National University, Canberra, Australian Capital Territory 2601, Australia
‡National Laboratory of Solid State Microstructures, Collaborative Innovation Center of Advanced Microstructures, School of Electronic Science and Engineering, Nanjing University, Nanjing 210093, People’s Republic of China

ABSTRACT: Atomically thin two-dimensional (2D) semiconductors have presented a plethora of opportunities for future optoelectronic devices and photonics applications, made possible by the strong light matter interactions at the 2D quantum limit. Many body interactions between fundamental particles in 2D semiconductors are strongly enhanced compared with those in bulk semiconductors because of the reduced dimensionality and, thus, reduced dielectric screening. These enhanced many body interactions lead to the formation of robust quasi-particles, such as excitons, trions, and biexcitons, which are extremely important for the optoelectronics device applications of 2D semiconductors, such as light emitting diodes, lasers, and optical modulators, etc. Recently, the emerging anisotropic 2D semiconductors, such as black phosphorus (termed as phosphorene) and phosphorene-like 2D materials, such as ReSe₂, 2D-perovskites, SnS, etc., show strong anisotropic optical and electrical properties, which are different from conventional isotropic 2D semiconductors, such as transition metal dichalcogenide (TMD) monolayers. This anisotropy leads to the formation of quasi-one-dimensional (quasi-1D) excitons and trions in a 2D system, which results in even stronger many body interactions in anisotropic 2D materials, arising from the further reduced dimensionality of the quasi-particles and thus reduced dielectric screening. Many body interactions have been heavily investigated in TMD monolayers in past years, but not in anisotropic 2D materials yet. The quasi-particles in anisotropic 2D materials have fractional dimensionality which makes them perfect candidates to serve as a platform to study fundamental particle interactions in fractional dimensional space.

In this Account, we present our recent progress related to 2D phosphorene, a 2D system with quasi-1D excitons and trions. Phosphorene, because of its unique anisotropic properties, provides a unique 2D platform for investigating the dynamics of excitons, trions, and biexcitons in reduced dimensions and fundamental many body interactions. We begin by explaining the fundamental reasons for the highly enhanced interactions in the 2D systems influenced by dielectric screening, resulting in high binding energies of excitons and trions, which are supported by theoretical calculations and experimental observations. Phosphorene has shown much higher binding energies of excitons and trions than TMD monolayers, which allows robust quasi-particles in anisotropic materials at room temperature. We also discuss the role of extrinsic defects induced in phosphorene, resulting in localized excitonic emissions in the near-infrared range, making it suitable for optical telecommunication applications. Finally, we present our vision of the exciting device applications based on the highly enhanced many body interactions in phosphorene, including exciton-polariton devices, polariton lasers, single-photon emitters, and tunable light emitting diodes (LEDs).

1. INTRODUCTION

The discovery of graphene in 2004 opened avenues for a new generation of 2D materials. It was followed by exploration of other 2D semiconductor materials such as transition metal dichalcogenides (TMDs),1,2 phosphorene,3 etc. Stronger interaction within lower dimensional systems leads to existence of robust many-body systems14 and quasi-particles5,6 in these atomically thin layered materials. These quasi-particles have been shown to exist in quasi-2D systems (quantum wells),7,8 2D materials4,5,9 and 1D carbon nanotubes (CNTs).10 The strong interaction is measured by “binding energy” of these quasi-particle systems. High binding energies allow these many body interactions between electrons and holes to be experimentally detected in various combined forms, such as excitons (electron and hole pair),11 trions (charged excitons),12 and biexciton (quantum combination of two-excitons: steady state or a trion and free charge: excited state).13 Binding energies of excitons (trions) have been theoretically and experimentally demonstrated to be in the range of 5–35 (1–5)
400–550 (20–34) meV in TMD monolayer,15,16 and 210–1100 (36–200) meV in CNTs.17–20 Detailed values of exciton, trion, and biexciton binding energies from various material systems from theoretical and experimental work have been summarized in Table 1.

However, the relatively low values of binding energies in quasi-2D and 2D systems only allow the exciton and trion photoluminescence (PL) peaks to segregate at cryogenic temperatures, barely resolvable at room temperature compared to their emission bandwidth.21 On the other hand, excitons and trions in 1D confined space (such as CNTs) exhibit much higher binding energies and the complete separation of exciton and trion PL peaks at room temperature because of further dimensionality reduction and reduced screening.1,10 However, the utilization of 1D CNTs for practical optoelectronic applications is critically limited by their small cross-sectional area.22 It is extremely difficult to assemble large-sized and optically uniform films composed of CNTs because of the varied distribution of chirality and other issues such as conversion of homogeneous templates in to long-chain CNTs at low temperatures.22,23 It has been a long-standing scientific challenge to optimize this trade-off between enhanced binding energies at confined dimensionalities and reduced cross-sectional areas, limiting the development of useful excitonic/trionic devices.

Table 1. Experimental and Theoretical Binding Energy Values (meV) for Various Quasi-Particles in Different Materials

<table>
<thead>
<tr>
<th>System</th>
<th>quasi-2D</th>
<th>2D</th>
<th>anisotropic 2D</th>
<th>1D</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>quantum wells</td>
<td>IL MoS₂</td>
<td>IL MoSe₂</td>
<td>IL WS₂</td>
</tr>
<tr>
<td>exciton</td>
<td></td>
<td>650±15</td>
<td>350±14</td>
<td>500±16</td>
</tr>
<tr>
<td>theory</td>
<td></td>
<td>6.6–33.6</td>
<td>18±10</td>
<td>30±17</td>
</tr>
<tr>
<td>trion</td>
<td></td>
<td>1.4–8.9</td>
<td>34±17</td>
<td>31±17</td>
</tr>
<tr>
<td>biexciton</td>
<td>exp T + C</td>
<td>2.13–2.24</td>
<td>69±13</td>
<td>58±13</td>
</tr>
<tr>
<td></td>
<td>X + X</td>
<td>70±18</td>
<td>60±15</td>
<td>65±18</td>
</tr>
<tr>
<td>theory</td>
<td>exp T + C</td>
<td>1.0–2.0</td>
<td>70±18</td>
<td>60±15</td>
</tr>
<tr>
<td></td>
<td>X + X</td>
<td>22±16</td>
<td>23±17</td>
<td>24±18</td>
</tr>
</tbody>
</table>

Note: T is trion, C is charge, and X is exciton. This distinction has been made to identify excited state (T + C) and steady state (X + X) biexcitons. This distinction has not been made for biexciton values from quantum wells and CNT. References for binding energies of CNTs and quantum wells have been cited in-text because of the large number of references. bThe value is from 3L phosphorene sample.
charged particles, which are determined by the level of Coulombic interaction between tropic 2D materials. The recently emerged anisotropic 2D materials, such as phosphorene, provides an elegant way to solve this challenge. Compared with other 2D materials, phosphorene shows strongly anisotropic properties, which results in quasi-1D excitons and trions in a 2D system. In this Account, we use the example of phosphorene to demonstrate the role of enhanced many body interactions in anisotropic 2D semiconductors, as compared to other 2D materials, such as TMDs. This enables a system that addresses the above-mentioned problem of the trade-off. High binding energies with large cross-section grant opportunities to use phosphorene in future optoelectronic devices, such as exciton-polariton devices, polariton lasers, tunable LEDs, and other excitonic devices based on exciton condensation. This Account is directed toward highlighting the role of dimensional confinement and emphasizes on various experimental techniques employed by us and other groups to study these many body interactions and quasi particles. At the end, we present our visions and prospect on the potential optoelectronic applications of those anisotropic 2D materials.

2. EFFECT OF DIMENSIONALITY AND DIELECTRIC ENVIRONMENT ON FUNDAMENTAL QUASI-PARTICLES

Many body effects, which result from the Coulombic electron–hole interactions, play a key role in determining their electronic transport and optical properties. The strength of electric fields between charged particles in a semiconducting material is determined by the level of Coulombic interaction between charged particles, which are affected by the dimensionality of the material and thus dielectric screening from the surrounding environment. The effect of the dielectric environment on the interaction of charges and the binding energy in various dimensionalities of semiconductors have been represented schematically in Figure 1. In a conventional bulk semiconductor, the electron–holes interact with each other with electric field lines passing through the dielectric medium of the material itself, causing significant dielectric screening, resulting in weak interactions among the charges. Thus, the binding energy of these quasiparticle/many-body systems originating from the coulomb interaction is almost negligible. In quasi-2D quantum wells, the interaction enhances as the charges are only confined in a quasi-2D space and the dielectric screening is diminished to an extent. In truly 2D materials, such as TMD monolayers, the dielectric screening to the interacting charges is considerably reduced due to the high localization of interacting charges within a single 2D plane. In quasi-1D excitons and trions, the stronger interaction leads to formation of stable excitons, trions, and biexcitons with higher binding energies as compared to quasi-2D systems. These quasi-particles have been demonstrated in various TMD materials, such as MoS$_2$, WS$_2$, MoSe$_2$, WSe$_2$, with binding energies of excitons as high as $\sim 0.6$ eV and are stable at room temperature. Simultaneously, existence of robust charge interactions combined with dimensional confinement lead to formation of higher order excitonic complexes, such as trions and biexcitons. Compared with other 2D materials, phosphorene shows strongly anisotropic properties, which results in quasi-1D excitons and trions in the 2D phosphorene (Figure 1). Because of the formation of quasi-1D trions and excitons, 2D phosphorene has ultrahigh binding energies of excitons ($\sim 0.8$ eV for monolayer phosphorene) and trions ($\sim 200$ meV), much higher than those values in TMDs. As the dimensionality is further reduced to true 1D with advent of CNTs, the reported binding energies of excitons ($>1$ eV) and trions ($\sim 200$ meV) were even higher than 2D systems due to further unidirectional confinement of charges.

Figure 2. (a) Phosphorene provides high binding energies similar to a true 1D system with a large 2D cross-sectional area. (b) Schematic diagram of an exciton-polariton interaction in a cavity with 2D material.
3. TIGHTLY BOUND EXCITONS AND TRIONS IN PHOSPHORENE

Binding energy is the key parameter that defines the extent of interaction between fundamental particles.\textsuperscript{11,28} Several theoretical and experimental techniques have calculated the binding energy of excitons, trions, and biexcitons. Table 1 summarizes the values of binding energies for various systems.

We successfully measured the binding energy of trions in a 3\textit{L} phosphorene sample, using a metal-oxide-semiconductor (MOS) device to tune the PL emissions via controlling the electrostatic doping with applied back gate voltage, as shown in Figure 3a and b. The 3\textit{L} phosphorene sample showed two emission peaks at \(\sim 1100\) and \(\sim 1300\) nm (Figure 3c–e), which were identified to be from excitons and trions, respectively. The relative intensity ratio of exciton/trion is tuned by gate voltage. When negative voltage is applied, positive charges are injected into the sample and hence the trionic emissions dominated and vice versa. We also demonstrated that optical charge injection can also be controlled with excitation power, to tune the trion density in 1\textit{L} phosphorene.\textsuperscript{24} Therefore, binding energy of trions in 3\textit{L} phosphorene was measured to be \(\sim 160\) meV, which is much larger than those values in TMD monolayers and is comparable to that in truly 1D CNTs (Table 1).

High-binding energy is attributed to anisotropic orientation of charged many-body complexes in phosphorene, which has been theoretically predicted as well.\textsuperscript{34} We confirmed this anisotropic excitonic and trionic emission from phosphorene using angle resolved PL spectroscopy.\textsuperscript{9,24} The PL intensity is highly dependent on the polarization angle of the incident light due to anisotropic absorption in phosphorene attributed to its puckered structure. We also observed that emission of excitonic emissions from phosphorene was also linearly polarized sharply. Thus, the many body complexes are mostly aligned along the armchair direction (as shown in Figure 1). This strong anisotropy results in higher binding energies which can result in several photonics device applications, which will be discussed in the later section.

4. PRODUCING AIR-STABLE MONOLAYER PHOSPHORENE

Degradation of phosphorene has been a long-standing challenge for the scientific community. It is easily oxidized in the presence of oxygen, moisture, and light.\textsuperscript{35} Several different passivation techniques have been demonstrated including,
passivation through coating by $\text{Al}_2\text{O}_3$\textsuperscript{36} by atomic layer deposition (ALD) technique\textsuperscript{37} and sandwiching between h-BN layers\textsuperscript{38} (Figure 4a). But, these techniques have been only partially successful in preserving fast degrading phosphorene flakes in the ambient environment.\textsuperscript{39} The h-BN encapsulation requires very complicated technique and has a low-throughput. Recently, we developed a novel technique (Figure 4d) combining oxygen plasma etching with subsequent $\text{Al}_2\text{O}_3$ deposition to preserve phosphorene flakes in pristine condition in ambient environment. This method has 2-fold advantages. It allows for controlling the thickness of phosphorene very precisely and effective preservation of the phosphorene samples. Oxygen plasma is used to etch through a thick flake of phosphorene. During the treatment, top layers of phosphorene are oxidized to become $\text{P}_x\text{O}_y$, which serve as protecting layers for phosphorene underneath. Further plasma etching allows oxygen plasma to penetrate this $\text{P}_x\text{O}_y$ layer and further oxidize the phosphorene layer underneath. After some time, a dynamic equilibrium is established so that etching rate and thickness of $\text{P}_x\text{O}_y$ become constant. This allows precise etching down to monolayer. Finally, an additional layer of $\text{Al}_2\text{O}_3$ is deposited over the etched phosphorene and $\text{P}_x\text{O}_y$ to protect it from oxidation. We found that mono- and bilayer samples which were fabricated by $\text{O}_2$ plasma etching can be coated with ALD $\text{Al}_2\text{O}_3$ without any further damage to the phosphorene samples under it due to the protective $\text{P}_x\text{O}_y$ layer on top of it. This technique allows forming a controlled air-stable few- to monolayered phosphorene samples, enabling its practical applicability in various device applications (Figure 4e).

5. DEFECT ENGINEERING IN PHOSPHORENE

Defect engineering in 2D materials has emerged a sturdy technique to modulate their optical properties for suitable optoelectronic applications. Single-photon emitters have been demonstrated from TMDs\textsuperscript{40} and h-BN\textsuperscript{41} recently. The defect states can be realized through oxidation, irradiation, and physical absorption.\textsuperscript{42} Phosphorene and other similar structure based anisotropic materials (ReS\textsubscript{2}, and ReSe\textsubscript{2}) offer a distinct advantage for defect engineering due to their puckered sp\textsuperscript{3}-like configuration. Defect induction in phosphorene is critical for triggering photon emission at new wavelengths, utilizing the layer dependent band gap in phosphorene from future optoelectronic devices point of view.

We induced defects in monolayer phosphorene using two distinctive methods.\textsuperscript{39,42} First, we used a plasma-enhanced chemical vapor deposition (PECVD) oxide substrate and deposited gold over it followed by phosphorene. PECVD oxide contained a lot of impurities and surface states, which were confirmed with FTIR spectroscopy. These surface states then act as trapping centers for excitons.\textsuperscript{39} Second, we introduced extrinsic oxygen defects in monolayer phosphorene using external oxygen plasma etching.\textsuperscript{39} Extrinsic defects as dangling "O" bonds are quite common in phosphorene and have been discussed in literature.\textsuperscript{43} Another form is the diagonal oxygen bridge (Figure 5a), which acts as potential trap state and is
quite stable. These surface defects can alter the optical properties of phosphorene and result in defect levels being created in the optical band gap of the materials (Figure 5b), which causes excitonic emissions from these localized states at lower energies than free exciton emission energies (Figure 5c). For defect engineering in monolayer phosphorene, we observed a free exciton emission at $\sim 720$ nm attributed to the free excitonic emission and low energy emission at $\sim 920$ nm (Figure 5d). The defect peak shows a sublinear growth in the integrated PL emission with increasing excitation laser power, thus establishing its defect nature. For defect emissions from TMDs that are only visible at cryogenic temperatures, the localized excitonic emissions at 920 nm showed much higher PL emission efficiency as compared to the free excitonic state. The overall quantum efficiency was extracted to be $\sim 33.6$ times higher than free excitonic emission. The enhanced PL emission yield could be attributed to the longer lifetime-radiative recombination of localized excitons in the trapping states. The defect states can function as quasi-zero-dimensional (quasi-0D) luminescence trapping centers with enhanced PL emission efficiencies. 2D phosphorene, with quasi-1D free excitons and quasi-0D localized excitons forms an interesting 2D−1D−0D hybrid system, which provides us a unique platform to explore the fundamental interactions at multidimensionalities. As suggested earlier, anisotropic materials due their specific molecular orientation are ideal candidates for defect engineering using any of the above-mentioned techniques. This is particularly interesting for phosphorene due to its layer dependent band gap, it could possibly lead to defect emissions in the infrared range. Most defect emissions in other TMDs and 1L phosphorene are $>1$ eV, which is in the visible range. Few-layered phosphorene samples can trigger emissions at much lower energies that are useful for telecommunication device applications.

6. OUR VISION: DEVICES BASED ON STRONG LIGHT MATTER INTERACTIONS IN PHOSPHORENE

The enhanced binding energies of these quasi-particles as discussed earlier is crucial for promising device applications. In this section, we will present our vision for such optoelectronic devices and their working principles based on phosphorene and other similar anisotropic 2D materials. Figure 6a depicts the key domains of device applications based on phosphorene directly linked with the interesting properties we have discussed earlier in this account. For example, high binding energy allows for its integration into a microcavity for electronically pumped exciton-polariton lasers. In microcavities created by Bragg’s mirror on either side of the 2D material (Figure 2b), a strong coupling of excitons and optical fields can be generated. 2D excitons and 2D optical...
modes in the strong coupling regime in these cavities gives rise
to new eigenmodes called excitons-polaritons. These can
enable study of quantum phenomenon such as Bose-Einstein
condensation, quantum vortices, and entangled photon pairs. Earlier reported exciton-polaritons have been based on
quantum wells, where these quasi-particles were only visible
at cryogenic temperatures. Recently, they have been reported
with TMD based materials in the microcavities owing to their
strong binding energy and direct band gap nature. Exciton-
polariton devices operating the infrared region are critical for
telecommunication applications and integration with conven-
tional silicon photonics. Recently, NIR exciton-polaritons were
reported using single walled CNTs. But, CNT-based devices
show large performance variation, since it is difficult to control
the position, alignment and chirality of the CNTs in the cavity
as discussed earlier. Phosphorene thus, provides a high binding
energy system, stable, perfectly controllable platform to
demonstrate such devices working the NIR region. Layer-
dependent band gap of phosphorene also allows flexibility of
choosing the emission wavelength range. As shown in the
Figure 6b, the microcavity consists of atomically thin phosphorene sandwiched between two SiO₂ layers, which is
placed between SiO₂/TiO₂ distributed Bragg’s Reflector (DBR)
mirrors. The cavity resonance can be controlled to match well
with exciton energy emitting from phosphorene sample. Polariton lasers can be made using the stimulated scattering
from exciton-polaritons that promises more energy efficient
generation of coherent light. The threshold energy for
coherent emission from a phosphorene polariton laser will be
much smaller as compared to a conventional laser.

Simultaneously, light emitting junctions based on TMD
materials have been demonstrated including the lateral p-n
ejunctions, vertical heterojunction diodes and vertical tunnel-
ing transistors. But, their emission wavelength as stated
above remains confined in the visible region. Phosphorene
based LEDs (Figure 6c) can act as potential sources for NIR
and even middle infrared (MIR) region emission for tele-
communication applications. Also, as we have demonstrated

Figure 6. (a) Envisioned research domains with anisotropic materials. (b) Schematic of the structure of planar microcavity composed of dual DBRs with the embedded phosphorene. (c) Schematic plot of the tunable phosphorene LED. Heterostructure band diagram shows the case for zero-bias and the case for a finite negative bias applied to the single layer graphene (SLG). BP: phosphorene. (d) Schematic diagram showing single-photon emissions from defect states in phosphorene.
earlier excitonic and trionic emissions from phosphorene can be controlled using external back gate tuning.\textsuperscript{24} Thus, phosphorene can enable tunable wavelength emissions from a single device, by controlling the back-gate voltage as shown in the schematic diagram Figure 6c. A vertically stacked heterojunction with graphene and phosphorene allows for electroluminescence (EL) from the whole device area, unlike Schottky junction or split-gate $p$–$n$ junction devices providing the benefit of atomically precise interfaces and barrier thickness.

Defect engineering in phosphorene as discussed earlier can lead to potential device applications.\textsuperscript{32} These defects act as efficient trapping centers, which when isolated can act as sources of single-photon emission. 2D materials have several key advantages to host single-photon emitters as they can negate the total internal reflection enabling high light extraction efficiency, enabling integration with photonic waveguides and plasmonic structures. They have been demonstrated recently with h-BN and TMD materials\textsuperscript{41} in which quantum defects are ascribed to localized excitons. But, for all single-photon emitters demonstrated in TMDs and h-BN operate in the visible range, limiting their application to quantum communication systems based on NIR fiber transmission. As we have demonstrated in our previous reports,\textsuperscript{39,42} defects can be implanted in phosphorene enabling low energy defect states by either substrate engineering or external oxygen plasma etching. PL emission from phosphorene can be tuned using defect integration with few layer phosphorene. Thus, making phosphorene few layers as an ideal host for single-photon emitters in NIR wavelength (Figure 6d). These defect emissions are in sharp contrast with defect emissions from TMDs, which are only visible at cryogenic temperatures.\textsuperscript{21} The defect emission from these defect/localized states is brighter (higher quantum efficiency) as compared to the free excitonic emission making it more suitable for NIR and MIR single-photon emission-based devices.

7. OTHER ANISOTROPIC MATERIALS

Apart from phosphorene, other anisotropic materials like GeSe/GeS,\textsuperscript{51} SnS,\textsuperscript{52} SnSe,\textsuperscript{53} ReSe$_2$, ReS$_2$,\textsuperscript{54} and 2D perovskites\textsuperscript{55} have also shown strong anisotropic optical properties. The theoretically calculated binding energies of the various fundamental quasi-particles are similar to those in phosphorene (Table 1), making them suitable for all the above-mentioned applications. Also, they are made of earth abundant and environmentally friendly elements making them suitable for optoelectronic applications.

8. CONCLUSIONS AND PROSPECTS

The ability to fabricate materials that are atomically thin has led us to explore stronger light-matter interaction that exist at that level. While reflecting on the key reasons for such strong interactions at the 2D limit, we highlighted the role of these interactions in enabling us to study the properties and applications of the quasi-particles such as excitons and trions in this account. Using our recent experimental observations on phosphorene, we highlight the importance of such anisotropic 2D semiconductors that provide a quasi-1D platform in a 2D system enabling even higher binding energies of excitons and trions. First, we calculated exciton and trion binding energies in phosphorene, which is one-order higher as compared to other TMD materials. Higher excitonic/trionic interactions in a quasi-1D anisotropic material enable exciting device applica-

- **AUTHOR INFORMATION**

**Corresponding Author**

*E-mail: yuerui.lu@anu.edu.au.*

**ORCID**

Ankur Sharma: 0000-0002-0863-1857

Yuerui Lu: 0000-0001-6131-3906

**Notes**

The authors declare no competing financial interest.

**Biographies**

Ankur Sharma is a Ph.D. student at NEMS lab in Australian National University (ANU). His research interests include 2D materials and device fabrication based on 2D materials.

Han Yan is a third-year undergraduate student at Research School of Engineering, ANU.

Linglong Zhang is a Ph.D. student at Nanjing University, China, and a visiting PhD research student at Australian National University.

Xueqian Sun is a postgraduate student at ANU.

Boqing Liu is a postgraduate student in NEMS lab in ANU.

Dr. Yuerui Lu is an Associate Professor and group leader of Nanoelectro-mechanical System (NEMS) Lab at ANU. His research interests include MEMS/NEMS, nanomanufacturing, renewable energy harvesting, biomedical novel devices, and 2D materials.

**REFERENCES**


**Accounts of Chemical Research**

**DOI:** 10.1021/acc.accounts.7b00594


