Unveiling Exciton Many-Body Interactions in WS$_2$ Single Crystal

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Abstract. Understanding the exciton many-body interactions and their recombination dynamics in transition metal dichalcogenides (TMDCs) are important for potential applications in optoelectronics and valleytronics. Herein, using ultrafast non-degenerate transient differential reflectance spectroscopy, we studied exciton interactions in WS$_2$ single crystal. Spectrally and temporally resolved studies revealed the strong interrelated excitonic interactions of A, B and C excitons and associated transient stark blueshift and broadening of exciton resonances. Additionally, we observed an unusual prolonged decay of direct band-gap exciton (A exciton) with fluence, which interprets the presence of trap state in the system. Our findings provide a comprehensive understanding of material’s intrinsic properties and exciton many-body physics which offers efficient pathways to optoelectronic applications based on TMDCs.

INTRODUCTION

Two-dimensional transition metal dichalcogenides (TMDCs) with unique properties like strong light-matter interaction (absorption ~ 20% per monolayer (ML)) [1], strong quantum confinement effects, direct to indirect bandgap crossover while going from monolayer to bulk and large spin-orbit coupling, etc. make them extremely attractive for fundamental studies of physical phenomena and for applications in spintronics, valleytronics, electronic and optoelectronics [1-3]. Particularly, the optical properties of TMDCs are mainly dominated by neutral and charged exciton states. These excitons and their correlated interactions have crucial role in optical and electronic response. Recently, WS$_2$ (having direct bandgap ~ 1.9 eV in ML limit, whereas it has indirect bandgap of ~ 1.3 eV in the bulk form) [4,5] got much attention because it offers several properties over other TMDCs like larger spin-orbit interaction because of heavier W-atom, higher mobility, strong valley polarization, tightly bound trions and higher binding energy due to reduced dielectric constant, etc. Hence, the study of exciton dynamics in such a system has a great potential in the technological fields.

Additionally, traps and defect states, caused by sulfur vacancies and dislocations, influence the recombination process of pump-induced carriers in TMDC [6]. The trap has an integral part in photoluminescence and several electronic device’s performances because the recombination via traps can affect the lifetime of carriers and thus hinders the flow of electron and hole in the electrical current circuits.

Strikingly, such studies mainly focus on atomically thin ML, few layers and their heterostructures but rare in single crystals. With this motivation, here we studied exciton many-body interactions in WS$_2$ single crystal by using ultrafast transient differential reflectance (DR) spectroscopy by employing above bandgap pump pulses at different fluences varying from 85 to 640 µJ/cm$^2$. Further, we identified the presence of trap states which alters the path of the charge carriers in recombination dynamics.

RESULTS AND DISCUSSION

To observe the excitonic transitions, we have recorded ground state optical reflectance (OR) by using an integrating sphere. Three sharp exciton peaks, termed as A, B and C exciton, detected at ~ 1.9, 2.3, and 2.6 eV, respectively, as shown in Fig. 1(a). A and B excitons arise from the splitting of the valence band minimum due to
strong spin-orbit coupling at K (K') valley, whereas, C-exciton is related to the transitions from various points close to Γ point of the Brillouin zone.

To investigate the nonequilibrium exciton dynamics in WS₂ single crystal, we used ultrafast transient DR spectroscopy and measured DR ($\Delta R/R = (R_{\text{excited}} - R_{\text{ground}})/R$) of a broadband probe (1.9-2.8 eV, that covers A, B and C excitons) at each pump-probe delay. DR is a technique that gives vision about the dynamics of charge carriers at ultrafast timescales. In the experiment, we used 400 nm (3.1 eV) pump excitation (pulse width 120 fs) to excite the sample at different fluences ranging from 85 to 640 µJ/cm². Initially, the pump generates hot carriers deep into the conduction band, and then electrons thermalize to their respective band minima’s by carrier-carrier and carrier-phonon scattering. This process occurs within few sub-ps timescales. Fig. 1(b) depicts the contour plot of WS₂ single crystal at 640 µJ/cm² pump fluence. To better understand, various cross-sections of the contour at different-probe delays have been taken (Fig. 1(c)).

The time-resolved study discloses essential features of exciton many-body interactions: (i) derivative feature at A and B exciton positions consisting of bleach at exciton position along with a blue-shifted photo-induced absorption (PIA), attributed to the stark effect (exciton-exciton repulsive interaction) [7], (ii) a relatively broad PIA between A and B excitons, (iii) a red-shifted absorption below A exciton position, associated with the trap states (Fig. 1(b-c)).

At initial time, hot exciton of the pump beam exerts Stark effect on the absorption of the subsequent probe beam exciton. In this condition, the DR spectra closely matches to the second derivative of the ground state OR spectra (Inset in Fig. 1(C) is representing the second derivative of the ground-state OR), which is consistent with our results. This excitonic interaction causes the blueshift and broadening of exciton resonances.

Figure 2(a) shows the spectral evolution at different pump fluences at 1 ps timescale. The pump fluence studies reveal that the broad PIA between A and B excitons (dashed box) is attributed to bandgap renormalization (BGR) since it appears only at higher fluences, the Coulomb interactions are powerfully screened because of the high carrier density and the exciton binding energy is reduced [8].
The temporal evolution of A-exciton bleach is shown in Fig. 2(b) at variable fluences. The decay of bleach was fitted using the bi-exponential function and the corresponding characteristic time constants are tabulated in Table 1.

**TABLE 1.** Fitting parameters of bi-exponential decay function of A-exciton.

<table>
<thead>
<tr>
<th>Pump Fluence (µJ cm$^{-2}$)</th>
<th>$\tau_1$ (ps)</th>
<th>$\tau_2$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>85</td>
<td>1.3 ± 0.1</td>
<td>59 ± 5</td>
</tr>
<tr>
<td>215</td>
<td>3.1 ± 0.3</td>
<td>64 ± 9</td>
</tr>
<tr>
<td>450</td>
<td>4.6 ± 0.4</td>
<td>71 ± 6</td>
</tr>
<tr>
<td>640</td>
<td>5.6 ± 0.8</td>
<td>96 ± 8</td>
</tr>
</tbody>
</table>

Because of defect states (sulfur vacancies, dislocations, etc.) within the bandgap region, the charge carriers are recombining via trap states. Therefore, the shorter time constant ($\tau_1$) is expressing the trapped carrier lifetime and the longer time ($\tau_2$) is associated with the recombination time of trapped carriers. The obtained time constants reveal that A exciton bleach strongly depends on fluence and shows unusually long decay at higher fluence, as manifested in Fig. 2(b). This phenomenon can be further explained by the schematic diagram shown in Fig. 3.

**FIGURE 3.** Schematic diagram of charge carrier recombination in WS$_2$ single crystal. At lower fluence decay is slow, whereas at higher pump fluences it is taking longer time because of carrier-carrier hopping within ET.

At lower fluence, carriers are rapidly captured by the defect states. Now, these defect states work as electron traps (ET). After that, these trapped carriers recombine to the conduction band minima. As we increase the fluence, the number of charge carriers increases in the ET. So the incoming charges take time to find the vacant place in the trap states. Therefore, the time $\tau_1$ is increasing with fluences. Now, a large number of charge carriers are present in the ET, so they start interacting with each other (shown by the yellow arrow) and decouple from the trap states, which further delays the time $\tau_2$ of the charge carriers.

**CONCLUSION**

In summary, we demonstrate the excitonic interactions of A, B and C excitons and their associated transient Stark effect induced blue-shift and BGR. The fluence dependent study reveals unusual slow decay of A exciton with the increase in fluence, indicating the recombination of charge carriers via trap states. Our results provide a standard for exploiting WS$_2$ in pristine or mixed, bulk, or confined form for potential application in the field of optoelectronics.

**ACKNOWLEDGEMENT**

The authors thank the Department of Physics, IISER Bhopal for financial support.
REFERENCES