Engineering Exciton Many-Body Interaction in Atomically Thin MoS$_2$

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Abstract. Atomically thin transition metal dichalcogenides (TMDs) have emerged as a leading semiconductor over the past decades due to their exceptional electronic, optoelectronic and quantum properties. Here, we have studied tuning of optical and electronic properties in CVD grown single- and few-layer MoS$_2$ by employing spectrally and temporarily resolved ultrafast transient absorption (TA) spectroscopy. By doing pump-fluence dependent measurement, we observed different optical response in two extreme fluence regimes. In the high pump-fluence regime above some critical carrier density, the system undergoes a transition from an excitonic bound state to the electron-hole plasma state, which is termed as Mott-transition. Our experimental findings show a drastic change in optical response in the very high pump fluence, which demonstrate a large bandgap renormalization of around 300 meV. Further, we have fitted TA for A and B exciton and found that both exciton energies red shifting with increasing pump fluence. These results indicate that atomically thin MoS$_2$ can be a promising material for phototransistors, quantum information processing, sensors, and light-harvesting devices.

INTRODUCTION

The exceptional properties like formation of bound electron-hole pair known as excitons, valley degrees of freedom, phonon bottleneck effect, auger recombination, topologically protected states have sparked broad research interest in TMDs ranging from valleytronics to superconductivity [1-3]. Interestingly, TMDs possess direct bandgap in the monolayer limit which shows crossover to indirect bandgap as a function of the number of layers mainly because the interlayer coupling changes the symmetry points in the brillouin zone at different rates [4]. These materials exhibit strong many body coulomb interactions, less dielectric screening which make them ideal candidate for correlated quantum phenomena as function of particle density [5]. Many body phenomena arising from interactions between charge carriers, quasi-particles (excitons, trions, bi-excitons) can lead to emerging phenomena such as bandgap renormalization (restructuring of band), multi-exciton generation, exciton-polariton condensation etc. Engineering quasiparticle and electronic bandgap is crucial for the application in solid state device where manipulation of electron is important, to name a few are information processing, light-harvesting devices, renewable energy and laser. These many body interactions can be strongly modified in the presence of very high electron-hole densities, offers to engineer optical response by injecting carrier in the excited state of the material.

In last few years, people have found some methods of tuning bandgap, for example, by applying electric and magnetic field, changing dielectric constant, altering chemical composition by external doping, or by applying high pressure. Most of these are perturbative and some of them change the pristine TMDC system [3,6-8]. So these are not suitable for most of the application. On the other hand, same can be done through altering many-body interaction by optically injecting large number of carrier via ultrashort intense laser pulse. To do that we have implemented ultrafast transient absorption (pump-probe) spectroscopy, and traced the optical response of MoS$_2$ in the excited state by injecting the carriers using different pump fluence. Our experimental results show a drastic change in the optical response over a critical carrier density (Mott-density), which demonstrate a bandgap renormalization of 300 meV. Further, we showed exciton energy position is continuously red shifting with increasing pump fluence.
EXPERIMENTAL DETAILS

To investigate the excited state properties of single and few-layer MoS₂, we implemented ultrafast transient absorption spectroscopy. In our experiment, we have taken laser pulses of pulse width 120 fs centered at 800 nm and repetition rate of 1 kHz from Spectra Physics Spitfire amplifier. The 800 nm pulse has been sent through a BBO crystal, which produces 400 nm pulse through second harmonic generation. These two beams of 400 nm and 800 nm have been separated using a dichroic beam splitter. The high energetic beam (400 nm) used as pump pulse and white light has been generated from the fundamental beam (800 nm) using CaF₂ nonlinear crystal, which is used to probe the sample over wide range of spectra. The pump and probe beam were spatially superimposed in the material and the probe beam was detected after passing it through the sample. We recorded change in absorption (ΔA (λ, t) = A_	ext{excited} - A_	ext{ground}) as a function of pump-probe delay and probe wavelength. Further, Ultraviolet-visible-NIR optical absorption spectroscopy was used to record ground state optical absorption. Deuterium lamp was used to generate UV light (160-400 nm) and tungsten-halogen lamp to produce Vis-NIR light (350-3500 nm). The source light beam was split into two beams, one passed through reference substrate or solvent and other passed through the sample (material + substrate). Then two beams collected by two detectors. Spectrometer scans all the wavelengths and it gives data of absorbance as function of wavelength.

RESULTS AND DISCUSSION

Our single-layer (SL) and few-layer (FL) MoS₂ films were grown on sapphire crystal by chemical vapor deposition (CVD). The Raman spectrum of SL and FL MoS₂ is shown in figure 1. Two sharp characteristic Raman modes are observed namely E₂g and A₁g exactly at the same position as the previously reported values [3] and they depend on number of layers. Further, according to the reports the difference of 19.2 cm⁻¹ of the two peaks confirm single layer of MoS₂.

![Raman spectrum of single and few-layer MoS₂](image)

The ground state optical absorptions of SL and FL MoS₂ are characterized by the three excitonic peaks namely A, B and C exciton at 1.88 eV, 2.02 eV and 2.85 eV respectively (for SL MoS₂) (see figure 3). The two lower lying excitonic peaks called A and B arises due to transition from spin-orbit splitting levels of valence band at K and K’ points in the hexagonal Brillouin zone and the higher energy peak in the band nesting region is called C exciton.
To trace the changes of optical and electronic properties in the excited state, fluence dependent spectrally and temporally resolved ultrafast transient absorption spectroscopy was implemented. The samples were excited using 100 fs pump pulse centered at 640 nm, just above the A exciton but below B exciton position, and probed using white light, covering all three exciton transitions. Moving from low fluence to high fluence regime highly modifies the interactions between the carriers present in the system, which in turn determine the optical and electronic properties. Spectral view of transient absorption at 0.78 ps for two pump fluences 4 µJ/cm² and 300 µJ/cm² is shown in figure 3(a) over wide probe wavelength 400 nm to 850 nm. At 4 µJ/cm² fluence pump pulse populates the lower energy optical band-edge exciton levels (A and B). However, the transition for C exciton is beyond the physics of direct transition at K and K’ valleys and it is well above the optical band edge, thus by band edge excitation and low pump fluence, inhibiting the population of C level by the pump light. Subsequent to the pump excitation, phase-space filling of A and B exciton states lead to reduction of ground state absorption resulting in the two characteristic bleach at A and B exciton position in the TA. For very high fluence 300 µJ/cm² regime drastic change is observed over the whole probe spectrum region. There is large absorption below C exciton down to below A exciton in addition to bleach signal at excitonic positions. Which is because of bandgap renormalization due to many-body interaction of large number carrier created by high pump fluence. Further, we have fitted the TA data for A and B exciton to monitor the exciton position with increasing fluence by the following equation-

\[ \Delta A = \sum_i Q^e_i \times \exp \left( -\frac{(\varepsilon - \varepsilon_{0i} - \delta_i)}{\omega^e_i} \right) - Q^g_i \times \exp \left( -\frac{(\varepsilon - \varepsilon_{00})}{\omega^g_i} \right) \]

Where, \( \varepsilon_{0i}, \delta_i, \omega^e_i, \) and \( \omega^g \) refers to the exciton position, energy shift, width of the exciton in the excited state and FWHM of the exciton in the ground state. From the fitting we have found that the both A and B exciton positions is continiously red shifted with increasing pump fluence upto 120 meV (wavelength converted to energy) for the highest pump fluence 300 µJ/cm² (figure 3(b)).
FIGURE 3. (a) Spectral view of transient absorption spectroscopy at fixed 0.78 ps for two extreme pump fluence 4 µJ/cm$^2$ and 300 µJ/cm$^2$. (b) Exciton energy shift of A and B exciton with variation of pump fluence, shows red shift with increasing fluence.

CONCLUSION

In summary, we have monitored electronic and optical response of CVD grown SL and FL MoS$_2$ in the excited state. We have found that above some critical pump fluence the system undergoes a transition from excitonic bound state to electron-hole plasma state which is termed as Mott-transition. In the electron-plasma hole regime, due to modified many-body interactions optical and electronic bandgap renormalizes hugely. These results open a path to engineer the bandgap for potential application of various solid state devices such as light-harvesting devices, phototransistor, sensor etc.

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REFERENCES