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Band nesting in semiconducting transition metal dichalcognide

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Abstract

Semiconducting two-dimensional crystals of transition metal dichalcogenides exhibit distinct electronic properties that are attractive for optoelectronics. We report on the effect of band nesting that leads to giant optical absorption and unique photocarrier relaxation in these materials.

1. Introduction

Since the successful isolation of graphene and other atomically thin crystals from the bulk layered compounds, renewed interest in the transition metal dichalcogenides (TMD) in their ultimate thickness regime led to the discovery of emerging properties that are drastically different from those of the bulk compound. Semiconducting 2D TMDs such as MoS_2 and WSe_2 exhibit strong band-gap photoluminescence (PL), circular dichroism due to valley polarization, and second harmonic generation to name a few [1].

Large absorption coefficient of TMDs in the visible frequencies makes them an attractive optoelectronic material. However, the origin of strong light-matter interaction in these materials has been elusive. Absorption spectra of MX_2 (M = Mo, W and X = S, Se) consist of characteristic band gap exciton peaks along with higher absorption features at higher energies. From differential reflectance spectroscopy, the peak in absorption by single layer MX_2 has been estimated to be as large as 30 %, significantly stronger than the light absorption by single layer graphene (2.3 %).

Recently, Carvalho et al. reported that such giant light-matter interaction is due to band nesting effect [2]. Nesting of the conduction and valence band in 2D systems leads to a singularity in the joint density of states (JDOS). Due to diverging JDOS, optical conductivity is strongly enhanced for the resonant condition. It should be noted that while singularities in the JDOS are present in common semiconductors and metals such as silicon and aluminum, divergence in optical conductivity occur only in low-dimensional materials.

While excitonic resonance near the band edge has been extensively studied, absorption at the band nesting energy, which typically occurs at ~1 eV above the optical band gap absorption, has not been studied in detail. Here, we investigate the effects of band nesting through absorption, photoluminescence (PL), and PL excitation (PLE) measurements of various monolayer MX_2 samples [3].

2. Results and Discussions

The absorption spectrum of monolayer MoS_2 exhibits excitonic resonance peaks at 1.8 and 2 eV and a strong absorption peak at 2.8 eV. The former two peaks are band gap excitonic transitions associated with the spin-orbit split valance band maximum and degenerate conduction band minimum at the K point of the Brillioun zone. Absorption at 2.8 eV is as large as 30 % suggesting that it is due to band nesting effect.

When monolayer MoS_2 is excited above its optical band gap, band gap PL (1.84 eV) is observed. Color-coded PLE map of monolayer MoS_2 is shown in Figure 1. The emission energy is independent of the excitation energy, suggesting that photocarriers fully relax to the band edge before radiative recombination.

We find that the PL emission intensity becomes weak as the excitation energy is increased above the optical gap. This is in striking contrast to the absorption features. The relative quantum yield of emission, which is obtained by normalizing the PLE intensity to the absorption, shows that the quantum efficiency of emission is strongly reduced when the excitation is in resonance with the band nesting energy.

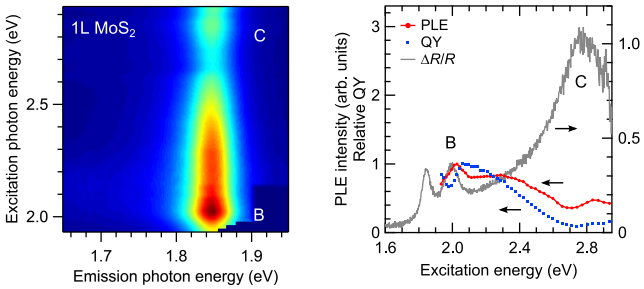

Fig. 1 Photoluminescence excitation and differential reflectance spectrum of mechanically exfoliated MoS_2 monolayer [3].

The energy dispersion of MoS_2 dictates that photo-excited electrons and holes relax with opposite momentum when the excitation is in resonance with the band nesting energy. That is, the electron-hole pairs created in the nesting region have the tendency to form indirect excitons. Our Monte Carlo simulations reveal that a large fraction of electron-hole pairs relax to different

valleys and hills, forming indirect excitons after thermalization. The radiative recombination rate of indirect excitons are typically longer than the rate of non-radiative recombination. Thus, the reduction in quantum yield can be explained by the formation of indirect exciton due to the band nesting.

3. Conclusions

Semiconducting transition metal dichalcogenides exhibit strong optical absorption owing to band nesting. Band nesting results in spontaneous formation of indirect excitons when the excitation is in resonance with the band nesting energy. Our experimental and theoretical studies highlight the unique consequence of the energy dispersion in 2D semiconductors. These findings highlight the possibility for harvesting hot exciton energies using these materials as the absorbing layers in optoelectronic devices.

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