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Dark-state impact on the exciton recombination of monolayer WS_2 embedded in van der Waals heterostructures

Takashi Kuroda[1*], Yusuke Hoshi[2,3], Kenji Watanabe[1], Takashi Taniguchi[1,3], Ryo Kitaura[4], and Tomoki Machida[3]

[1] National Institute for Materials Science, 1-1 Namiki, Tsukuba 305-0044, Japan
[2] Tokyo City University, 8-15-1 Todoroki, Setagaya-ku, Tokyo 158-0082, Japan
[3] Institute of Industrial Science, University of Tokyo, 4-6-1 Komaba, Maguro-ku, Tokyo 153-8505, Japan
[4] Department of Chemistry, Nagoya University, Nagoya 464-8602, Japan
*Phone: +81-(0)29-860-4194, E-mail: kuroda.takashi@nims.go.jp

Abstract

The luminescence yield of transition metal dichalcogenides (TMD) frequently suffers from the formation of long-life dark states, which include spin-forbidden states, excitons with inter-valley transitions, and those with a large center-of-mass momentum, located outside the light cone of the dispersion relation. Rapid relaxation from the bright exciton states to the dark states suppresses the efficiency of light emission. In addition, radiative recombination of excitons is heavily influenced by Auger-type exciton-exciton scattering, that leads to another non-radiative recombination channel at high densities. Here, we clarify that Auger-type scattering is promoted not only between (bright) excitons but between excitons and long-life dark states. We studied the luminescence dynamics of monolayer WS_2 capped with hBN for broad time ranges spanning from picosecond to millisecond, using carefully designed pump-and-probe techniques. We observed that luminescence quenching associated with Auger-type scattering occurs at 1-100 μs time scales, which thus correspond to the lifetime of dark states in monolayer WS_2 at room temperature. The broad distribution in the measured time constants implies the impact of various types of long-life states on the exciton annihilation.

1. Introduction

The high yield light emission associated with exciton recombination makes transition metal dichalcogenide (TMD) monolayers as a unique platform to demonstrate various exciting physics. Mechanisms behind the strong light emission of TMD monolayers include 1) strong interband transitions as both conduction and valence bands consist of the metal *d* orbitals, and the absorption coefficients of TMD commonly exceed 10% per monolayer depending on wavelength, and 2) large exciton binding energies on the order of 0.5 eV, which assures the stable formation of excitons even at room temperature. The observation of ultrafast spontaneous emission that had a few ps decay time confirmed the enhanced exciton oscillator strength. However, it is also commonly accepted that standard monolayer TMD samples exhibit a quantum yield lower than 1%, possibly limited by the presence of crystalline defects, the impact of various dark states, which include intervalley excitons, spin-forbidden states, and excitons with non-zero center-of-mass momentum, and Auger-type scattering that results in nonradiative exciton annihilation.

Recently we observed that Auger-type exciton annihilation is greatly suppressed by encapsulation of WS_2 monolayers with hexagonal boron nitride (hBN), which is a prominent substrate for 2D materials thanks to reduced surface roughness, low background-carrier densities, and improved transport properties [1]. The improved surface homogeneity of TMDs/hBN leads to the formation of delocalized excitons, which are homogeneously dispersed over the 2D plane. In contrast, TMDs supported on a common class of substrates (such as SiO_2) tend to have dense localization centers, which enhance the contact-type exciton-exciton scattering.

In this work, we focus on the microscopic process of Auger-type exciton annihilation. We extend the measurement time scale up to to 1 ms with constructing a luminescence-based pump-and-probe setup. Hence, we clarified Auger-type scattering between excitons and other long-life dark states whose lifetimes are distributed in 1-100 μs time scales.

2. Results and discussions

We used a CVD grown WS_2 monolayer supported on an SiO_2 substrate, that showed a significant luminescence quench at high excitations [1]. It is capped by an hBN film to avoid optical damage during the experiment. The detail of the sample preparation is described in [1]. All experiments were performed at room temperature.

Figure 1 shows the decay curves of the neutral exciton luminescence line observed at 1.99 eV for different excitation powers. Here, we excited the sample using ultrashort pulses, which have a temporal width of 2 ps, a wavelength of 540 nm, and a repetition of 76 MHz, generated by an optical parametric oscillator. A standard confocal microobjective setup allowed us to collect the luminescence signals from a focusing region with a diameter of ~1μm. Then, the signals were temporally analyzed using a synchronously scanning streak camera with a resolution of 2 ps. For sufficiently low excitation (100 nW), the signal shows a single exponent decay with a time constant of 420 ps. With increasing excitation power to 1 μW, the signal decays faster with a time constant of 100 ps. This is a common signature for the Auger-type exciton scattering. Further increase in excitation power to 10 μW reveals a short time constant of 30 ps.

Note that the luminescence intensity at time origin (0 ps in this figure) is nearly proportional to the excitation power, while the decay constant monotonically changes. Hence, the high excitation curve goes below the low excitation curve at a particular time depicted by the blue vertical arrows. The observed behavior suggests the luminescence intensity does not simply follow the transient population of excitons generated by each pulse. Instead, the luminescence curve is governed by previous pulses, that accumulates the population of long-life states whose lifetimes are longer than the excitation period, i.e., 13 ns. Thus, the strong luminescence quench is associated with incoherent scattering between excitons and the long-life dark states.

Figure 2 shows the time evolution of luminescence signals excited by square-wave optical pulses with a time width of 50 μs and a duty ratio of 10%, generated by an acousto-optic modulator (AOM, 200 MHz center frequency). The luminescence signals were counted by an avalanche photodiode and a multichannel scaler with a minimum bin of 5 ns.

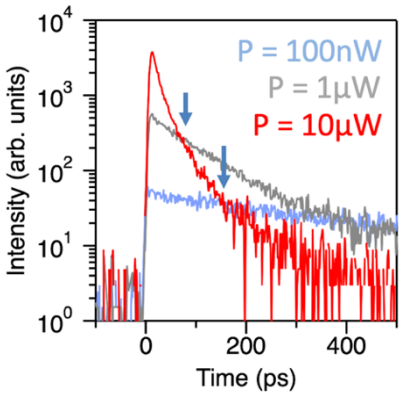

Fig.1 Picosecond luminescence dynamics: Time-resolved luminescence signals of monolayer WS_2 capped by an hBN film, excited by 2 ps pulses with a repetition of 76 MHz. They were measured at room temperature.

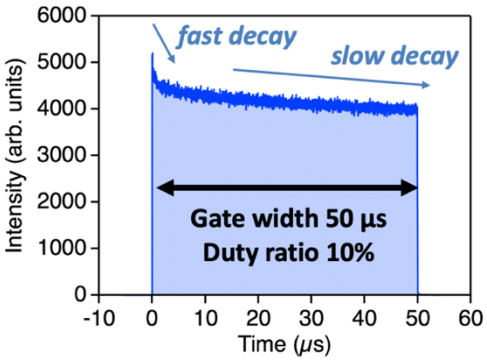

Fig. 2 Microsecond luminescence dynamics: Time evolution of photoluminescence signals of monolayer WS_2 excited with square wave pulses with a time width of 50 μs and a duty ratio of 10%.

They reveal a significant luminescence reduction with time, i.e., progressive increase in the probability of Auger-type scattering between excitons and accumulated dark states. The decay curve consists of a fast component with a time scale shorter than 1 μs, and a slow component with a time scale longer than 10 μs.

To confirm the accumulation of dark states, we introduced a pump-and-probe type measurement, where we operated AOM with controlled pulse sequences. Figure 3 shows the result of this measurement, which reveals the recovery of luminescence intensity with an average time constant of 4 μs, which thus corresponds to the lifetime of dark states. We also observed the presence of longer-time components that have a 250 μs recovery time. The attribution of each state will be discussed in the presentation.

3. Conclusions

We confirmed that exciton-exciton annihilation in monolayer WS_2 is associated with not only direct scattering between two excitons, but scattering between an exciton and other long-life charge complexes, i.e., dark excitons. We revealed that the dark excitons have distributed lifetimes on the order of 10 μs in monolayer $WS2/SiO_2$ at room temperature.

Acknowledgements

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References

[1] Y. Hoshi et al., Phys. Rev. B 95, 241403(R) (2017).

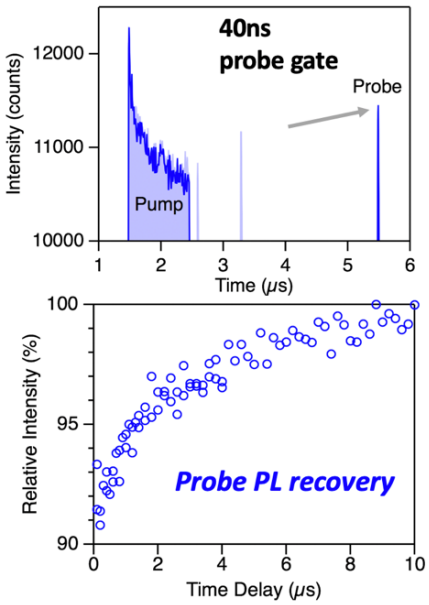

Fig. 3 Microsecond pump and probe measurement. The top panel shows the time trace of luminescence signals excited by 1-μs pump pulses and 40-ns probe pulses, which are delayed systematically. The bottom panel shows the intensity of probe-excited luminescence as a function of delay time.