Energy splitting between 2*s* and 2*p* excitons in hBN-encapsulated monolayer WSe_2

Satoshi Kusaba[1], Yoshiki Katagiri[1], Kenji Watanabe[2], Takashi Taniguchi[2], Kazuhiro Yanagi[3], Nobuko Naka[1] and Koichiro Tanaka[1,4]
[1]Department of Physics, Kyoto University, Sakyo-ku, Kyoto, 606-8502 Japan
[2]National Institute for Materials Science, Tsukuba, Ibaraki, 305-0044 Japan
[3]Department of Physics, Tokyo Metropolitan University, Hachioji, Tokyo, 192-0397 Japan
[4]Institute for Integrated Cell-Material Sciences, Kyoto University, Sakyo-ku, Kyoto, 606-8501 Japan

***Abstract*—Optical sum-frequency generation spectroscopy reveals a clear dipole-inactive 2*p* exciton transition in hBN-encapsulated monolayer WSe_2 under excitation with broadband picosecond near infrared laser pulses ($\hbar\omega = 0.56 \sim 1.3$ eV). We find that the transition energy is 8.8 ± 0.1 meV lower than that of 2s exciton, which is consistent with the numerical calculation result using the Keldysh potential.**

I. INTRODUCTION

Transition metal dichalcogenides (TMDs) are promising 2D materials in optoelectronics. In the monolayers of these materials, strong Coulomb interactions occur due to the reduced dielectric screening [1]. The electrons and holes form stable nonhydrogenic exciton states with a few hundred meV binding energy. Hence the excitons play an important role in optical and electrical properties even at room temperature. Recently, it has been found that high-quality hBN-encapsulated monolayer samples show exciton transitions with narrow linewidths, which enables us to observe clear excited exciton states, such as 2*s*, 3*s* and 4*s* states, in photoluminescence or absorption spectra [2-4]. Clear observation of the exciton Rydberg series allows us to determine the material parameters such as the band-gap energy and the exciton binding energy. So far, *p*-series excitons have not been investigated sufficiently because they are electric dipole inactive and cannot be accessed by 1-photon absorption or emission spectroscopies, whereas the *s*-series excitons have been well studied by conventional methods.

In this work, we performed sum-frequency generation (SFG) spectroscopy [5,6] in hBN-encapsulated monolayer WSe_2 to elucidate the forbidden 2*p* exciton state. The 2p peak is observed in the low energy side of 2s peak with the splitting energy of 8.8 ± 0.1 meV, which is consistent with the numerical calculation.

II. EXPERIMENT

An hBN-encapsulated monolayer WSe_2 heterostructure sample was prepared by mechanical exfoliation of bulk WSe_2 (2D Semiconductors Inc.) and bulk hBN crystal grown by chemical vapor deposition (CVD). The sample was characterized by optical contrast and photoluminescence measurements. Figure 1 shows the schematic of the experimental setup. The sample was set on the cold-finger of a Gifford-McMahon cooler and cooled down to 16 K. We used a picosecond supercontinuum light source (spectral range: 0.56 ~ 3.1 eV, repetition rate: 40 MHz). For 1-photon excited photoluminescence (1P-PL) measurements, visible excitation light with linewidth as narrow as 1 nm was obtained by a home-built subtractive-mode double monochromator. For SFG spectroscopy, only the near-infrared (NIR) excitation light (0.56 ~ 1.30 eV) was extracted using a dichroic mirror and a long-pass filter to prevent the 1-photon absorption process. The excitation light was focused onto the sample using a reflective objective. The emission light from the sample was collected by the same objective and led to a spectrograph equipped with a liquid nitrogen cooled Si charge-coupled device (CCD) camera.

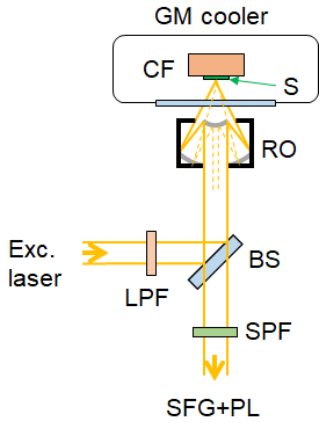

Fig. 1. Schematic of the experimental setup of SFG spectroscopy (LPF: long-pass filter, BS: beam splitter, RO: reflective objective, S: sample, CF: cold finger, GM cooler: Gifford-McMahon cooler, SPF: short-pass filter).

III. RESULTS

Figure 2(a) shows 1P-PL spectrum obtained at 16 K under 1.97 eV excitation. In addition to the strong 1*s* exciton peak at 1.698 eV (not shown in Figure 2(a)), we observed the 2*s* exciton hot luminescence peak at 1.828 eV. Figure 2(b) shows emission spectrum under NIR supercontinuum irradiation. In addition to the 1*s* and 2*s* peaks, a new peak was observed at 8.8 ± 0.1 meV lower than the 2*s* exciton peak, which was absent in the 1P-PL spectrum. We measured power dependence of these peaks and confirmed almost square dependence for both peaks. Therefore, these peaks should appear through a second-order nonlinear process (SFG and/or 2-photon excited photoluminescence (2P-PL)). We attribute the new peak to the 2*p* exciton state because of the following reasons: First, the 2*p* exciton should have lower energy than the 2*s* exciton in monolayer TMDs due to the reduced dielectric screening [7]. Second, according to the group theory analysis, *p*-series excitons are forbidden for the 1-photon absorption/emission but allowed for the SFG process [5]. It has been known that SFG signals have a clear polarization dependence (or crystal

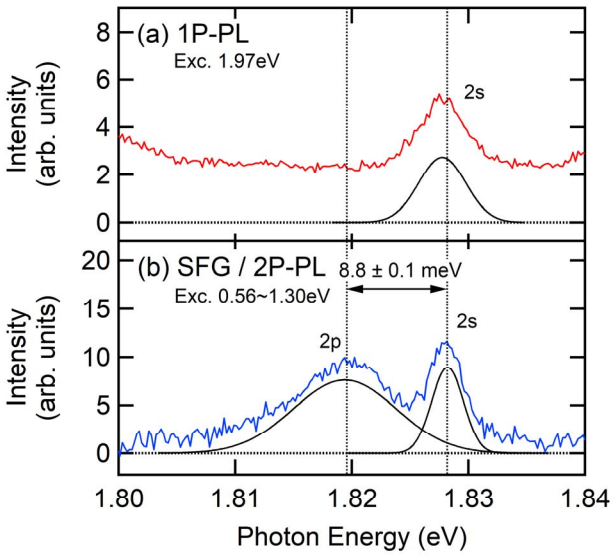

Fig. 2. (a) Photoluminescence spectrum obtained under 1.97 eV excitation in hBN-encapsulated monolayer WSe_2 at 16 K. (b) Sum-frequency generation and 2-photon excited photoluminescence spectrum in the same condition as in (a). Black lines in (a) and (b) show best-fit Gaussian functions.

orientation dependence) in this material [8]. We measured the emission polarization of the new peak and concluded that the new peak is originating not from PL but from the SFG process. We cannot observe any fine structure of the 2*p* exciton that was predicted by previous theoretical analysis [9]. It is noteworthy that linewidth of the 2*p* exciton peak is much broader than that of the 2*s* exciton peak, suggesting a faster decay channels of the 2*p* exciton state.

IV. Numerical Model Calculations

To explain the exciton peak positions obtained by our experimental data, we carried out numerical model calculations using the Keldysh potential, that is believed to describe the Coulomb interaction in a 2D electron-hole pair system confined between dielectric materials [1-4,10]:

$$V_K(r) = -\frac{e^2}{8\varepsilon_0 r_0}\left[H_0\left(\frac{\kappa r}{r_0}\right) - Y_0\left(\frac{\kappa r}{r_0}\right)\right], \qquad (1)$$

where H_0 and Y_0 are the zeroth-order Struve and Neuman functions. We used the screening length $r_0 = 4.5$ nm following the previous study [2] and the effective dielectric constant $\kappa = 4.29\varepsilon_0$ of the surrounding material (hBN) so that the calculated 1*s*-2*s* difference matches the experimental result. The experimental and calculated relative energy positions of the 1*s*, 2*s* and 2*p* states are shown in figure 3. The calculated value of the 2*s*-2*p* splitting energy is 10.9 meV. This agrees closely with our experimentally measured value of 8.8 ± 0.1 meV. The slight difference between calculated and experimental values is presumably due to the finite hBN layer thickness or the energy splitting of the 2*p* exciton level [9].

V. Summary

We performed SFG spectroscopy in hBN-encapsulated monolayer WSe_2 and observed the 2*p* exciton peak at 8.8 ± 0.1 meV low energy side of the 2*s* exciton peak. We also carried out numerical model calculation using the Keldysh potential

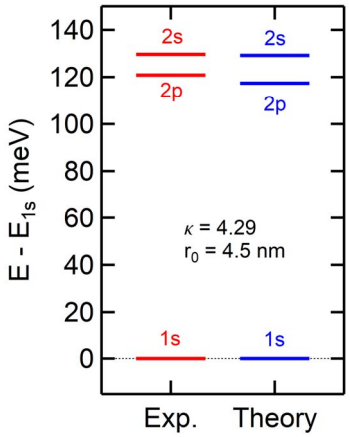

Fig. 3. Experimental and theoretical results of the relative energy positions of the 1*s*, 2*s* and 2*p* exciton states.

and the calculated value of the 2*s*-2*p* splitting energy was 10.9 meV, in close agreement with the experimental result.

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