Variation of photoluminescence spectral line shape of monolayer WS₂

Yongjae Kwon[a], Kangwon Kim[a], Wontaek Kim[b], Sunmin Ryu[b,c], Hyeonsik Cheong[a,*]

[a] *Department of Physics, Sogang University, Seoul 04107, South Korea*
[b] *Department of Chemistry, Pohang University of Science and Technology (POSTECH), Pohang 37673, South Korea*
[c] *Division of Advanced Materials Science, Pohang University of Science and Technology (POSTECH), Pohang 37673, South Korea*

A B S T R A C T

The origin of the variation of photoluminescence (PL) spectra of monolayer tungsten disulfide (WS₂) is investigated systematically. Dependence of the PL spectrum on the excitation power show that the relatively sharp component corresponds to excitons whereas the broader component at slightly lower energy corresponds to negatively charged trions. PL imaging and second harmonic generation measurements show that the trion signals are suppressed more than the exciton signals near the edges, thereby relatively enhancing the excitonic feature in the PL spectrum and that such relative enhancement of the exciton signals is more pronounced near approximately armchair edges. This effect is interpreted in terms of depletion of free electrons near the edges caused by structural defects and adsorption of electron acceptors such as oxygen atoms.

1. Introduction

Two-dimensional (2D) layered transition-metal dichalcogenides (TMDs) have attracted much interest recently owing to remarkable 2D physical properties that may be useful for novel device applications. For example, field effect transistors based on TMDs have shown a high on-off ratio [1]. Also, strong luminescence from many monolayer TMDs due to a direct band gap and a large exciton binding energy [2–6] may also be advantageous for nanoscale optoelectronic devices such as light-emitting devices [7,8], photodetectors [9], or solar cells [10]. In addition, an optical logic gate by selective control of light helicity [11] has been demonstrated by utilizing the valley degree of freedom in TMDs [12–15]. Tungsten disulfide (WS₂) is one of the most studied TMDs and is frequently used to study valley effects or to make heterostructures with other TMDs.

The optical properties of TMDs are often dominated by the excitonic features because of large exciton binding energies owing to strong Coulomb interaction due to reduced screening in 2D materials [2–5]. Thanks to the strong Coulomb interaction, trions, a bound state of an exciton and an electron or a hole, are often observed with binding energies of tens of meV's [2,16]. Because of the excitonic nature of the photoluminescence (PL), PL characterizations are used routinely to identify the number of layers or to estimate the quality of TMDs samples, etc. However, the reported PL spectra of monolayer WS₂ sample show a large variation [17,18] unlike the case of MoS₂. At room temperature, monolayer WS₂ usually have strong PL signals at ~ 2.0 eV. Whereas some samples show a broad PL peak, others have a sharp peak

at a slightly higher energy. In this paper, we try to clarify the origin of the variations by analyzing the excitation power dependence and spatial variation of the PL spectra of monolayer WS₂ samples.

2. Materials and methods

Monolayer WS₂ samples were prepared by mechanically exfoliating single crystal WS₂ flakes (HQ Graphene) onto Si substrates with a 285-nm SiO₂ layer. The number of layer was confirmed by combination of optical contrast and Raman spectroscopy. Raman and PL measurements were carried out using a home-built confocal microscope system using the 488-nm (2.54 eV) line of an Ar⁺ laser and the 514.4-nm (2.41 eV) line of a diode-pumped-solid-state (DPSS) laser, respectively. The laser beam was focused onto a sample by a 50 × objective lens (0.8 N A.). The scattered light was collected and collimated by the same objective lens, dispersed by a Jobin-Yvon Horiba iHR550 spectrometer (2400 grooves/mm for Raman and 300 grooves/mm for PL), and detected with a liquid-nitrogen-cooled back-illuminated charge-coupled-device (CCD) detector. The laser power was kept at 50 μW to avoid damaging the sample, except for the excitation power dependence measurements. A microscope-based polarized second harmonic generation (SHG) system, described elsewhere in detail [19], was used to determine the crystallographic orientation of the sample. Briefly, a 140-fs Ti:sapphire laser (Coherent, Chameleon) with a wavelength of 820 nm and a repetition rate of 80 MHz was focused onto a 1.0-μm spot with a 40 × objective. The SHG signal centered at 410 nm was collected by same objective lens and guided to a spectrograph (Andor, Shamrock
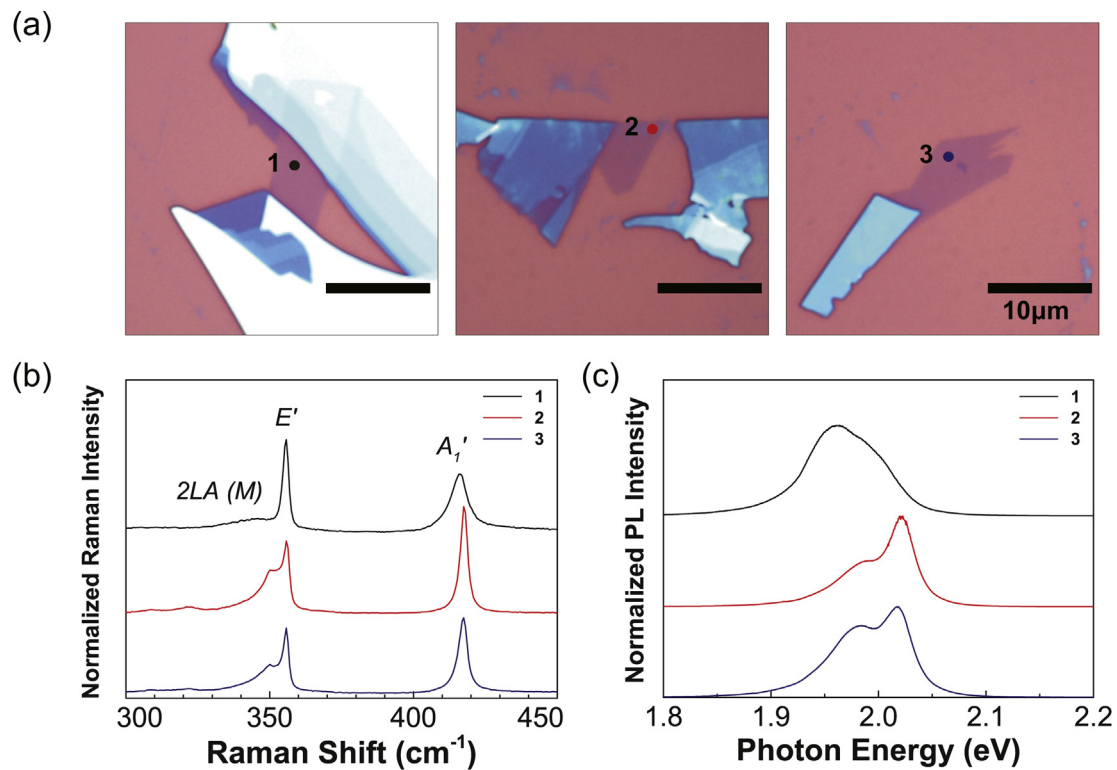
Fig. 1. (a) Optical microscope images of monolayer WS_2 samples. Normalized (b) Raman and (c) PL spectra of monolayer WS_2 for the three samples in (a).

303i) equipped with a thermoelectrically cooled CCD (Andor, Newton). The angle between the WS_2 lattice and the laser polarization was varied by rotating the sample on a rotation stage with accuracy better than 0.2°. Parallel or perpendicular polarization of SHG signal was selected by an analyzer in front of the spectrograph.

3. Results and discussion

3.1. Variation of PL spectra from monolayer WS₂ samples

Fig. 1(a) and (b) show optical images and Raman spectra of three monolayer WS_2 samples. The E′ and A_1′ modes, which correspond to the E_{2g}^1 and A_{1g} modes due to intra-layer vibrations along the in-plane and out-of-plane directions in bulk WS_2, are observed at ~ 356 and $\sim 417 \, cm^{-1}$, respectively [20,21]. The separation between the two peaks ($\sim 61 \, cm^{-1}$) is consistent with the literature value for monolayer WS_2 [20–22]. Fig. 1(c) shows PL spectra of the three samples. There is a large variation in the peak position and the line shape. Residual strain or variations in doping density influence the PL spectrum of TMDs materials [23,24]. For example, the A_1′ mode, which is sensitive to doping [23], is slightly red-shifted in the Raman spectrum of sample 1 with respect to those in the other two spectra, which indicates that there is some doping. The different line shapes also indicate that the contributions of different components of the PL vary among samples. In order to find the origin of the PL spectrum variations, we studied sample 3 in more detail.

3.2. Excitation power dependence of PL

Fig. 2(a) shows the dependence of the PL spectrum from sample 3 on the excitation laser power from 5 to 200 μW. At low excitation powers, the spectrum is dominated by a relatively sharp peak at ~ 2.02 eV. A much weaker signal is seen at a lower energy of ~ 1.98 eV. As the excitation power increased, the lower energy peak grows much faster than the higher energy peak. The PL spectra were deconvoluted

using a double-Lorentzian function, and the results are summarized in Fig. 2(b) and (c). The intensity reversal and the peak position shift are consistent with reported behaviors of exciton and trion peaks from WS_2. The PL signal from trions, bound states of two electrons and a hole or one electron and two holes, usually increase more rapidly than the exciton PL [25,26]. Furthermore, the trion states tend to redshift at higher excitation power due to the shift of the Fermi level [25–28]. Because WS_2 samples without intentional doping are n-type [29], the trions are negatively charged. Therefore, we assign the higher energy peak to the exciton (X) recombination and the lower energy one to the negatively charged trion (X⁻) recombination.

3.3. Spatial variation of PL

In order to study the spatial variation of the PL spectrum from monolayer WS_2, we carried out PL imaging of sample 3. Fig. 3(a) show PL spectra taken from the area marked by a white-dashed box in Fig. 3(b) in 1-μm steps. Results of deconvolution into double Lorentzian are also shown. The relative intensities of exciton and trion signals vary: trion seems to be stronger in the middle of the sample. For better comparison, we carried out PL imaging of the area in Fig. 3(b) in 0.5-μm steps and deconvoluted the exciton and trion components from each spectrum. Fig. 3(c) and (d) show the intensity maps of exciton and trion PL signals, respectively, and Fig. 3(e) is the ratio of the former to the latter. Although the intensity is stronger in the middle part of the sample for both exciton and trion signals, the exciton signal is relatively stronger near the edges, which is what we see in Fig. 3(a). Due to structural defects near the edges, it is reasonable to expect that the PL signal is reduced near the edges. In order to see if the enhancement of the exciton to trion ratio at the edges has any correlation with the orientation of the edges, we carried out second harmonic generation (SHG) measurements. Since the intensity of the SHG signal is strongly sensitive to the relative angle between the principal axis of the crystal and the polarization of the incident light [30–33], the crystallographic orientation of the sample can be determined from polarized SHG