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Strong Photoluminescence Fluctuations in Laser-Thinned Few-Layer WS_2

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We present results of μ-Raman and μ-photoluminescence study of few-layer WS_2 flakes that have been locally thinned down by a focused laser beam. The Raman spectroscopy measurements prove that the investigated flake was locally thinned down to a monolayer. Interestingly, μ-photoluminescence experiments allowed us to observe huge intensity fluctuations at the boundary of laser-thinned region. Similar effects were found at the edges of a WS_2 bilayer flake, which has not been subjected to laser-thinning. The origin of the observed time evolution of the photoluminescence response is discussed in terms of potential fluctuations resulting from light-induced changes of the charge state of defects.

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1. Introduction

Transition metal dichalcogenides (TMDs) have recently become a worldwide subject of intensive optical studies. One of the astonishing properties of these materials is that their band structures undergo a transformation from indirect to direct band gap when the number of layers is decreased from a bulk form to a monolayer (1 ML), which is accompanied by a substantial growth of the photoluminescence (PL) intensity [1, 2]. Since up to now there are no well-established procedures of deterministic synthesizing of 1 ML TMDs, an efficient and reliable method of fabricating them from bulk flakes would be very desirable. Moreover, deterministic production of 1 ML can be very useful from the application point of view, such as nanotransistors or optical markers [3, 4].

We study the effect of laser thinning process employed to WS_2 flakes. The same procedure was successfully used in case of MoS_2 [5]. At the same time, several works demonstrated arising of single-photon emitters in WSe_2 structures [6–8], which probably were related to imperfections in crystalline structure. However, there are no works focused on the influence of defects formed during laser-thinning process, on the PL response of the investigated flakes.

2. Sample and experimental setup

The WS_2 flakes were obtained on a Si/(320 nm)SiO_2 substrate by exfoliation of bulk crystals.

Laser thinning process was carried out with frequency-doubled Nd:YAG laser ($\lambda = 532$ nm), which provided power density $P = 4 \times 10^7$ W/cm^2. Each point was exposed to laser radiation for about 15 min. We found that the laser-thinning process happened much slower and weaker than in MoS_2, which may be associated with higher decomposition point of WS_2 crystals [9]. Diameter of a laser spot was about 0.6 μm. Raman spectroscopy and PL measurements were performed by means of the same laser, but the power density was 3 orders of magnitude smaller. Renishaw inVia system was used for the Raman spectroscopy carried out at 300 K. PL measurements were done with the aid of T6400 Horiba Jobin Yvon system at liquid helium temperature.

3. Experimental results and discussion

In order to investigate homogeneity of a sample, its quality, and number of thinned layers, we performed the Raman spectroscopy measurements.

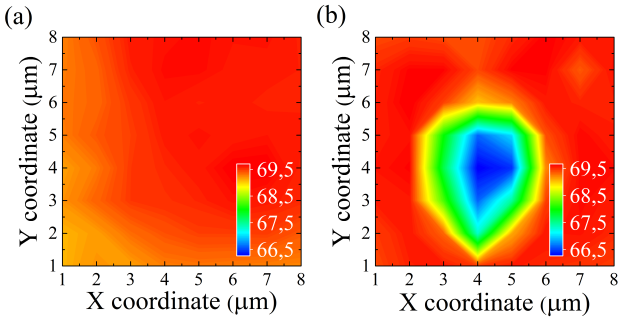

Fig. 1. Spatially-resolved maps of the Raman shift difference of the region (a) before and (b) after thinning process.

To determine number of layers, we focused on a Raman shift difference between A_{1g} mode, which is observed around 420 cm^{-1} and E_{2g} mode, apparent approximately at 350 cm^{-1}. It is known that the Raman shift difference between those two peaks decreases with number of layers [10, 11]. It can be seen in Fig. 2a and b that the

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investigated region before thinning is homogeneous (the difference varies only about 0.1 cm^{-1}), while after laser thinning the Raman shift difference ranges from around 66.5 cm^{-1} to almost 70 cm^{-1}. The obtained value of the difference in the center of thinned region indicates that the flake thickness was reduced to a monolayer.

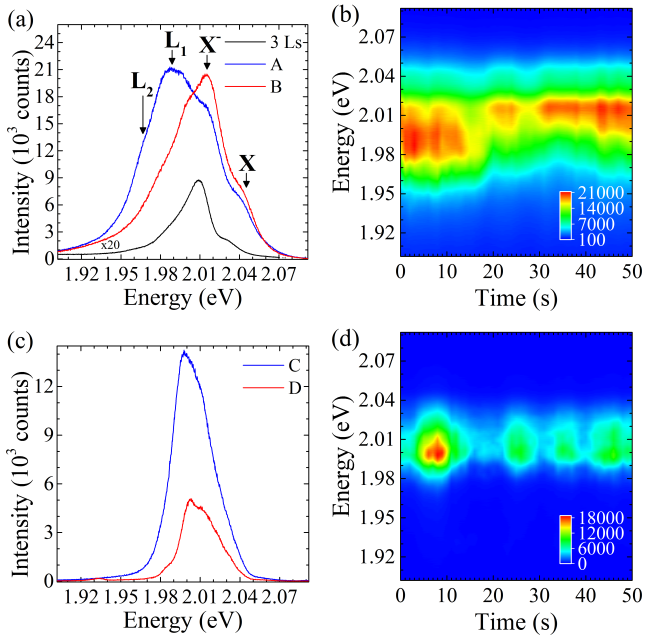

Fig. 2. (a) PL spectra before thinning procedure (3 MLs) and at two different moments of time (A: $t = 3$ s and B: $t = 4$ s) and (b) time evolution of PL intensity map measured on the thinned flake, (c) PL spectra at two different moments of time (A: $t = 6$ s and B: $t = 16$ s) and (d) time evolution of PL intensity map measured on the bilayer/substrate edge.

In Fig. 2a, we compare three PL spectra measured on the same place before thinning procedure [unthinned trilayer (3 MLs)] and after in two different moments of time (A and B). The difference between these three spectra is apparent. We observe enormous intensity increase, which is expected for the 1 ML WS_2 due to the indirect to direct band gap transition (see Ref. [12]). Moreover, it was reported that PL spectra of 1 ML WS_2 consist of several emission lines, which are associated with recombination processes of the neutral (X), negatively charged (X^-), and localised/defect-bound (L_1, L_2) excitons [13, 14]. In our case, those transitions occur at around 2.05 (X), 2.02 (X^-), 1.99 (L_1), and 1.97 eV (L_2), which is in agreement with previously reported values in Ref. [14]. Note that in earlier papers only X and X^- emission lines were attributed [15–17]. In Fig. 2b we show PL intensity map created from 51 spectra, each taken with 1 second delay. As can be seen, all of mentioned transitions were observed, however their intensities strongly fluctuate when the total PL intensity does not change too much. We excluded the influence of experimental setup on obtained results, e.g. variations of sample position, because its stability was checked in our previous experiments. The observed phenomena can be explained in terms of photo-induced charge fluctuations and trapping of excitons by defects. Charge state change time of ms order of magnitude is not unusual — in case of deep traps with activation energy much higher than kT value charge state change may take even minutes [18–20]. We found similar fluctuation effect at the edge between bilayer (2 MLs) and substrate (see Fig. 2c and d). However, the magnitude of this effect on the total PL intensity is much stronger on the 2 MLs/substrate edge. It may indicate that this emission is mainly associated with the recombination of the defect-bound excitons (compare the energy position of lines in Fig. 2a and c).

In order to investigate these effects we use correlation method [21]. This technique was already used, particularly to study the charged state of given excitonic lines in single quantum dots (QDs), which also exhibited the fluctuation effect under quasi-resonant excitation [22].

The function is as follows:

$$r(m,n) = \frac{\sum_i (I_m^i - \langle I_m \rangle)(I_n^i - \langle I_n \rangle)}{\sqrt{\sum_i (I_m^i - \langle I_m \rangle)^2 \sum_i (I_n^i - \langle I_n \rangle)^2}}, \qquad (1)$$

where $r(m,n)$ is correlation coefficient with values ranging from –1 to 1. I_m^i and I_n^i are intensities in the spectrum i measured at energies m and n, respectively, moreover $\langle I_m \rangle$ and $\langle I_n \rangle$ are mean intensities over all spectra at energies m and n, respectively.

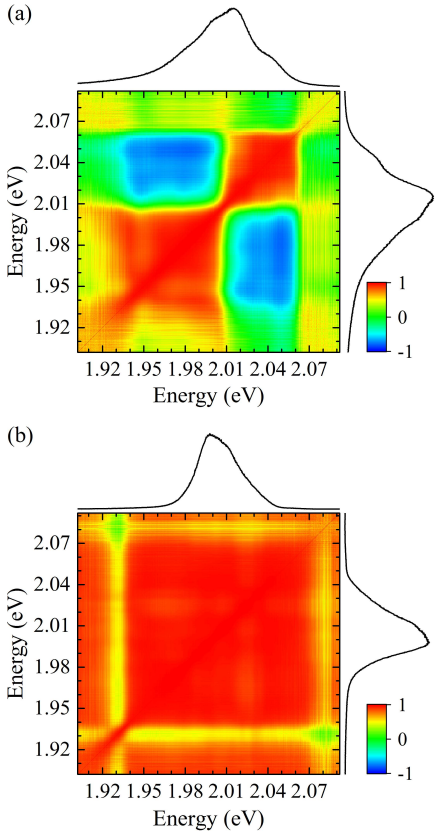

Fig. 3. Maps of the correlation matrix for a number of consecutively measured PL spectra (a) of the thinned flake and (b) of the 2 MLs/substrate edge.

The results of correlation coefficient function are presented in Fig. 3 for both studied cases: the laser-thinned flake and the 2 MLs/substrate edge. Red parts are associated with positive correlation, so the situation in which increase in intensity of one part of the spectra is accompanied by increase of intensity in the other part of the spectra. While blue parts indicate negative correlation, so increase in one part of the spectra is accompanied by decrease of intensity in the other part of the spectra. We observed that the negative correlation occurs between defect-bound (L_1 and L_2) and free (X and X^-) excitonic emission lines. However, positive correlation is visible for each of defect-bound excitonic emissions (between L_1 and L_2) and free (between X and X^-) excitonic transitions. This effect can be explained in terms of competition between different radiative processes. It is analogous to various charge state of QD, however, in this case it is related to free or defect-bound excitons. Moreover, we observe quite distinctive behaviour in 2 MLs/substrate edge: whole correlation matrix is positive, with some parts that resemble no correlation and can be assigned to noise. It shows that some charge fluctuations of defects may occur on the edges of the flakes due to activation of non-radiative recombination channels.

4. Conclusions

We showed that laser thinning can be useful method to produce monolayer of WS_2 crystal in deterministic way, which was further proved by means of the Raman spectroscopy. However, significant resistance of the material to undergo laser thinning proves to be an important issue. Moreover, we found that defects created during this process influence recombination in 1 ML WS_2. Analysis of correlation between transitions provided us with more information about nature of phenomena, which causes this effect. More research are needed to study a specific effect of numerous types of defects on optical properties of WS_2 and other materials.

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