Substitutional oxygen activated photoluminescence enhancement in monolayer transition metal dichalcogenides

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ABSTRACT Atomically thin transition metal dichalcogenides (TMDCs) are intriguing semiconductors for photonics and optoelectronics, and therefore enhancing their photoluminescence (PL) efficiency is crucial for these applications. Many efforts have been contributed to enhancing the PL performance of monolayer TMDCs, yet the complexity between the microstructure and the PL efficiency has hindered the manipulation of their PL properties. Here we demonstrate that the PL intensity of the monolayer TMDC can be enhanced by nearly one order of magnitude with a ~20% narrower spectral linewidth after a pre-activation plateau using laser irradiation in ambient environment. Combined experimental and theoretical studies reveal that low-power laser irradiation generates many sulfur vacancy clusters, which are subsequently filled up by oxygen, and the lattice substitutional oxygen clusters induce the dramatic PL enhancement of monolayer WS₂. Such PL enhancement phenomenon is found to be universal for other monolayer TMDCs, and thus would benefit their versatile optical applications.

Keywords: two-dimensional materials, transition metal dichalcogenides, photoluminescence enhancement, laser, oxygen

INTRODUCTION

Two-dimensional (2D) semiconducting transition metal dichalcogenides (TMDCs) with the formula of MX₂ (M for transition metals and X for chalcogenides, such as S, Se, or Te) are promising candidates for photonic or optoelectronic applications due to their direct bandgaps ranging from near-infrared to visible light [1–5], strong light-matter interactions [3,6], valley polarization [7–9], etc. One important characteristic for optical applications is the excitonic photoluminescence (PL), which is strongly associated with atomic level structures of materials [10,11]. Many efforts have been devoted to improving the PL performance of monolayer TMDCs through defect

engineering, while based on somehow two opposite strategies [1,12–27]. The first strategy is to make TMDCs close to intrinsic state by reducing or passivating defects [12–14], electrostatic gating [15], or surface engineering [18]. This strategy enhances the PL performances of TMDCs by strongly suppressing the non-radiative recombination pathway caused by the structural distortions. The second strategy is making the structures of TMDCs more defective to enhance their PL performances [1,16,19–21,23–25,27]. For example, He *et al.* [24] reported increased PL intensity of monolayer WS₂ when oxidized in ambient conditions. Tongay *et al.* [16] reported the generation of anion vacancy in exfoliated TMDCs, which is believed to be an effective method to manipulate their PL intensities. In another study, Nan *et al.* [23] reported increased PL intensity at the crack region of monolayer MoS₂. So far, the inconsistency between these two strategies indicates complicated structure-PL relationship in such monolayer semiconductors. Therefore, bridging the gap between the macroscopic PL performance and the microscopic structural perturbations (e.g., point defects and substitutional impurities) is essential for understanding the PL property of monolayer TMDCs.

Here we observed an anomalous PL enhancement of monolayer WS₂ by continuous low-power laser irradiation. The PL intensity of monolayer WS₂ increases by nearly one order of magnitude, and the spectral linewidth decreases by ~20%. Interestingly, such PL enhancement also accompanies a pre-activation plateau in which the PL remains almost unchanged. Scanning transmission electron microscopy (STEM) results show that the increased formation of sulfur vacancies during the pre-activation plateau induced by laser irradiation plays an important role in activating the PL enhancement process. Density functional theory (DFT) calculations further reveal that the laser-induced sulfur vacancy clusters can be filled up by oxygen, and elaborate that these oxygen substitutional defect clusters dramatically increase the emission energy of defective WS₂ at a critical concentration. We have also observed similar

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anomalous PL enhancement phenomena (plateau and sudden increase of PL) in other TMDC monolayer materials such as WSe₂, MoS₂, and MoSe₂, verifying the universality of substitutional oxygen in the PL enhancement process.

EXPERIMENTAL SECTION

Sample preparation

Monolayer TMDCs (MoS₂, MoSe₂, WS₂, and WSe₂) were mechanically exfoliated from their bulk crystals (2H phase, HQ graphene) onto the surface of 285 nm SiO₂/Si substrates. Monolayer WS₂ was transferred onto the TEM grid for characterization using a dry-transfer method with a polyethylene terephthalate (PET) stamp [28]. Briefly, a PET stamp was used to pick up the as-exfoliated monolayer WS₂ and put in contact with a Ted Pella Quantifoil TEM grid (657-200-AU, 2 μm holes) at 60°C. The PET was then removed by immersing the stamp and TEM grid in dichloromethane overnight.

Optical measurements

As an excitation source, a 532-nm (2.33 eV) laser beam was focused on monolayer TMDCs with a spot diameter of ~1 μm. The PL and Raman spectra of monolayer TMDCs were collected by a Horiba confocal Raman spectrometer (LabRAM HR Evolution) in reflection geometry. For time-dependent PL measurements, the integrated time for each spectrum was set to be 0.1 s unless otherwise claimed and the time intervals for two spectra were also set to be 0.1 s (the minimum value our setup can provide). The laser power was set to be 2 μW unless otherwise claimed. The PL mappings of monolayer TMDCs were done before and after high-temperature thermal annealing at ~300°C in air.

Data handling

The PL spectrum of monolayer WS₂ was fitted using two Voigt functions based on the consideration of exciton and trion components. The resultant parameters were used as initial guess parameters for the batch peak fitting of the time-dependent PL spectra. The fitting tolerance was less than 10⁻⁶. The deconvoluted exciton and trion spectra were displayed in a 2D color plot manner to show their evolution under laser irradiation.

Atomic-resolution STEM measurements

Atomic-resolution high-angle annular dark field STEM (HAADF-STEM) images were acquired with a double-aberration-corrected STEM (Titan Cubed Themis G2 300) operated at 60 kV. The semi-convergence angle was about 30 mrad and the semi-collection range of the STEM image was around 54–168 mrad.

First principles calculations

All calculations were performed using the DFT as implemented in the Vienna *ab-initio* Simulation Package [29]. The exchange-correlation functional was chosen in the form of generalized gradient approximation, as parameterized by Perdew, Burke, and Ernzerhof [30]. The projector augmented wave [31,32] pseudopotentials of W (6s²5d⁴) for W, S_GW (3s²3p⁴) for S, O_GW_new (2s²2p⁴) for O were used, together with a plane wave cutoff of 310 and 521 eV for systems without and with oxygen, respectively. The supercell size was 5 × 5 × 1 of the primitive cells of WS₂ with *a* = *b* = 15.89 Å, and the Brillouin

zone was sampled with a 12 × 12 × 1 Γ-centered mesh.

RESULTS AND DISCUSSION

We first exfoliated monolayer TMDCs (2H phase) using the Scotch-tape method and studied their PL property upon laser irradiation (Fig. 1a, see the EXPERIMENTAL SECTION for details). Taking monolayer WS₂ as an example, it was mechanically exfoliated onto silicon substrates with a 285-nm-thick oxide layer. The monolayer flake was identified by optical microscopy image contrasts and further confirmed by PL spectra, as shown in Fig. S1 in the Supplementary information. The as-exfoliated monolayer WS₂ was continuously irradiated by laser in air and its PL spectra were continuously monitored (see details in the EXPERIMENTAL SECTION). A representative record of the PL spectrum evolution is shown in Fig. 1b in a 2D colorplot form. The color scale corresponds to PL intensity, a horizontal line traces the PL intensity changes at the given emission energy, and the vertical line cut represents the PL spectrum at the given time. As an example, Fig. 1c shows how the peak intensity in the PL spectrum of monolayer WS₂ evolves along the black dashed lines (Fig. 1b) at ~1.99 eV. It clearly shows that the exposure of monolayer WS₂ to low-power laser irradiation slightly increases the PL intensity to a steady state, which then remains in the same plateau for ~80 s, similar to the results in previous reports [17,33]. Strikingly, we observed a sudden intensity increase starting at ~88 s, which has not been reported. This anomalous sharp increase in PL intensity reaches its peak value at ~91 s. The inset in Fig. 1c further compares the PL spectra of monolayer WS₂ recorded at 0 s (blue line) and 91 s (red line). The peak intensity at 91 s is ~8 times higher and the peak position redshifts by 10 meV in comparison with the initial PL spectra at 0 s. The redshift of the peak position possibly suggests the formation of laser-induced defective states near the band edge of WS₂. The PL intensity was followed by a subsequent decrease due to obvious damage of the sample.

The PL spectra of monolayer WS₂ can be well fitted using two Voigt functions based on the consideration of exciton and trion components [34], as shown in Fig. S2. The resultant evolution of decomposed exciton and trion components are summarized in Fig. S3. Both the intensities of exciton (Fig. S3a) and trion components (Fig. S3b) reach a maximum at 91 s, showing a similar enhancement feature to the total PL spectra. In addition, the linewidth of the exciton component (red line, Fig. 1d) increases slightly when the irradiation time elongates and suddenly drops by ~20% at ~91 s when the PL peak intensity reaches a maximum. Similarly, the peak position of exciton (blue line, Fig. 1d) redshifts slowly under laser irradiation and blueshifts slightly at ~91 s. However, trion shows a different behavior (Fig. 1e). The linewidth of trion keeps almost unchanged and the peak position blueshifts by ~10 meV when the PL peak intensity reaches a maximum. These observations indicate that the laser irradiation induces defective states before the PL enhancement and suppresses these defective states thereafter. Overall, our results show that continuous laser irradiation can modulate the PL performance of monolayer WS₂.

To shed light on the origin of the anomalous PL intensity change of WS₂, we monitored its structural alternation at atomic level using aberration-corrected HAADF-STEM at five time nodes labeled as b–f during stages I to III in Fig. 2a (reproduced from Fig. 1c). The corresponding results are shown in Fig. 2b–f, where single (V_{1s}) and double sulfur vacancies (V_{2s}) are marked

Figure 1 PL enhancement of monolayer TMDC under laser irradiation. (a) A schematic illustration of the PL enhancement for monolayer TMDC under laser irradiation. (b) Time-dependent PL spectrum of monolayer WS₂ under continuous laser irradiation. The PL intensity evolution along the black dashed line is shown in (c). (c) PL peak (~1.99 eV) intensity evolution of monolayer WS₂ under continuous laser irradiation. Inset: two representative PL spectra at different irradiation times: blue for 0 s and red for 91 s. (d, e) The spectral linewidth (red) and peak position (blue) evolution of exciton component (d) and trion component (e) under continuous laser irradiation. The dashed lines in (d) and (e) label the time when PL intensity reaches a maximum.

by yellow and red circles, respectively. Fig. 2b shows that monolayer WS₂ has ~1.6% V_{1S} and ~2.0% V_{2S} defects at its pristine stage (Stage I). No significant change of defect density is observed at b (~1.6% V_{1S}) and c (~2.1% V_{1S}), indicating that the PL enhancement in Stage I is irrelevant with the defect density, which possibly originates from the removal of adsorbed contaminations from the surface of monolayer WS₂ by laser heating. In the steady pre-activation stage (Stage II), the defect density of V_{1S} increased to 4.9% at point d (Fig. 2d), and further to 6.2% at point e (Fig. 2e). Similar increase is also seen for V_{2S}, from 1.9% to 5.6% as irradiation time increases, which is summarized in Fig. 2g. Overall, during Stage II, the density of sulfur vacancies gradually rises with irradiation time, while the linewidths (peak position) of both exciton and trion increase (redshift) slowly, indicating that laser-induced sulfur vacancies modulate the PL performance of WS₂, but have a trivial contribution in the enhancement of PL intensity. On the other hand, during/after the activation of the sharp increase of PL (Stage III), we find that further laser irradiation may dramatically increase the density of sulfur vacancies. This is evidenced in point f, where the generation of many sulfur vacancies finally results in the formation of holes with the diameter ranging from several to tens of nanometers, as shown in Fig. 2f. These holes grow to a much larger size (even to ~80 nm as shown in Fig. S4) at the end of the Stage III, and lead to a significant drop in the effective emission areas and the resultant decrease of the PL intensity. The spectrum features of both exciton and trion show little variation after

the PL intensity reaches a maximum, as indicated by the black dashed lines in Fig. 1d, e, it is reasonable to investigate the representative structural feature of stage III at point f.

The spectral feature of exciton (and trion) shows different trends before and after the PL enhancement process (Fig. 1d, e), indicating the evolution of sulfur vacancies to nano-sized holes is the key factor to understand the sharp PL enhancement process. Fig. 3a–c show characteristic HAADF-STEM images of monolayer WS₂ at stage III, where nano-sized holes with different diameters ranging from 0.8–80 nm are identified clearly (for more details, see Fig. S4). Small holes with ~1 nm size usually have W-terminated edges, as shown in Fig. 3a, which are related to the loss of WS₆ cluster possibly through multiple double-sulfur vacancies nearby [35]. Fig. 3b, c show large holes with diameters of ~2 and ~30 nm (see Figs S5 and S6 for more information), whose edges are also mainly terminated by W atoms. At the hole edges, particles with brighter contrast than tungsten atoms are often observed, as guided by the blue arrows in Fig. 3a–c (see Fig. S5). The chemical composition of these brighter clusters is determined to be tungsten oxides by electron energy loss spectroscopy (EELS), where the characteristic onset of the oxygen K edge can be clearly distinguished as shown in Fig. 3d. The existence of tungsten oxides in irradiated WS₂ is further verified by energy dispersive X-ray spectroscopy (EDX) mappings as shown in Fig. 3e, f, where the spatial distribution of O, S, and W elements is marked by red, green, and blue colors, respectively. The S and W elements are evenly distributed in the

Figure 2 Laser-induced structural variation of monolayer WS₂ upon time increasing. (a) The irradiation time-dependent PL peak intensity of monolayer WS₂. Three stages can be identified as Stage I, II, and III. (b–f) HAADF-STEM images corresponding to different irradiation times as labeled in (a), yellow and red circles indicate the single and double sulfur vacancies, respectively. (g) The sulfur vacancy concentration ($C(V_s)$) at different time nodes, as labeled in (a).

undamaged area of WS₂, while oxygen element is distributed in the whole area of WS₂ and accumulated near the edges of holes, overlapping with the bright cluster region. The formation of the holes suggests a metastable sulfur vacancy agglomeration before structural breaking, while the vacancy bonded oxygen indicates the oxygen molecule in air may further involve in the vacancy agglomeration and lattice reactions within WS₂. The observation of holes and bonded oxygen provides hints to understand the sharp activation of the PL enhancement process.

To reveal the underlying mechanism of the laser-induced PL modulation, we carried out first-principles calculations based on DFT to examine the electronic properties of WS₂ with and without defects. Fig. 4a shows the representative sulfur vacancy V_{ns} (n denotes the number of sulfur atoms) and the oxygen-substituted sulfur O_{ns} , both of which are major defects as suggested by the HAADF-STEM images in Figs 2 and 3. In Stages I and II, the temperature of WS₂ is expected to be relatively low and only a limited number of V_s are formed. Fig. 4b shows that V_s exhibits PL peaks significantly (> 0.5 eV) lower than the pristine one. For instance, V_{6s} shows a PL peak about 1.3 eV below the pristine PL peak, which is not captured in our PL spectrum. The low defect concentration and low PL peak posi-

tion explain the fact that the PL spectra remain nearly unchanged in the observed energy region in Stages I and II.

As heat accumulates at the WS₂/SiO₂ interface during the continuous laser irradiation on monolayer WS₂ due to the low heat dissipation rate of silicon dioxide [36], the temperature of WS₂ is expected to increase accordingly with time. At the beginning of the activated PL enhancement (Stage III), the temperature of WS₂ is supposed to reach a critical value at which the thermal energy is comparable to the formation energy of sulfur vacancy. Further increase of the temperature results in a nearly exponential increase of V_s concentration as schematically shown in Fig. 4c. Since filling chalcogen vacancies with oxygen atoms is thermodynamically preferable [37], the dramatic increase of sulfur vacancies will lead to a dramatic formation of O_{ns} , even clusters (e.g., O_{6s}). Fig. 4b shows that O_{ns} exhibits PL peak about 0.3 eV below the pristine PL peak. Because a lower PL peak corresponds to a smaller bandgap and thus more excited electrons, the PL intensity of O_{ns} is also envisioned to increase dramatically. These explain qualitatively the red-shifted PL peak positions and the dramatic increase of PL intensity as observed in Fig. 1c. We also performed calculations on the electronic structures of nano-sized holes with S- or O-termi-

Figure 3 The structure of the nano-sized holes in WS₂ formed during the Stage III. (a–c) Representative HAADF-STEM images of monolayer WS₂ after laser irradiation, of which holes have different diameters (labeled as D). The blue arrows indicate the particles coming from the holes during laser irradiation. The edges of these holes are predominately composed of W atoms (bright). (d) HAADF-STEM image of the edge of holes. Inset: EELS spectrum shows clearly the K edge for oxygen, demonstrating the existence of tungsten oxides in bright particles. (e, f) HAADF-STEM (e) and corresponding EDX mapping images (f) of laser-irradiated WS₂. The red, green, and blue in (f) indicate the EDX mapping of O, S, and W, respectively.

Figure 4 Theoretical interpretation for laser-induced PL modulation of monolayer WS₂. (a) Structural models of a perfect and several types of defective monolayer WS₂. (b) Dependence of relative PL peak position on defect types. (c) Schematic relationship between V_S concentration and temperature.

Figure 5 Oxidization-induced PL enhancement of monolayer WS₂. (a) The optical microscopy image of exfoliated WS₂ monolayers on a SiO₂/Si substrate. (b–h) PL intensity mappings of as-exfoliated WS₂ flakes after heating on a hot plate for different times (b: 0 min, c: 0.5 min, d: 1.5 min, e: 3.5 min, f: 8.5 min, g: 23.5 min, h: 55 min). (i) The PL peak intensity changes when heated for different time periods. It could be observed that the PL intensity increases to the maximum value followed by a decrease of intensity.

nated edges, as shown in Fig. S7. These nano-sized holes with S- or O-terminated edges show much lower emission energy than that of pristine WS₂, which indicates that they did not contribute strongly to the PL enhancement process. In the latter part of stage III, the elevated temperature of WS₂ is supposed to induce excessive defects that boost the formation of nano-sized holes (Fig. 2f), leading to a sharp decrease of PL intensity (Fig. 1c).

The proposed mechanism and its generality were further verified by our controlled experiments in N₂ environment and the thermal annealing of WS₂ and several other TMDCs in air. The low-power laser irradiation of monolayer WS₂ in a sealed chamber filled with N₂ did not show significant PL enhancement even for long time irradiation (see Fig. S8), indicating a significant role of oxygen in the PL enhancement. Fig. 5a shows an optical microscopy image of monolayer WS₂ that was thermally annealed at 300°C for a certain period of time. The corresponding PL intensity mapping results are shown in Fig. 5b–h. Fig. 5i traces the PL intensity changes in Fig. 5c–h, demonstrating a similar PL emission activation trend (after a pre-activation plateau then sudden increase). We found that the oxidization-induced PL enhancement was universal for four typical monolayer TMDCs (MoS₂, WS₂, MoSe₂, and WSe₂), as demonstrated in Fig. S9.

CONCLUSION

In summary, we observe that the PL intensity of monolayer WS₂ can be enhanced by nearly one order of magnitude when irradiated by laser, in premise of a pre-activation PL plateau.

Atomic-scale STEM results indicate that the laser irradiation creates a large amount of sulfur vacancies, and suggest lattice oxygen substitution and related defect clustering due to the formation of oxidized compounds and nano-sized holes with oxygen-bonded edges. DFT calculations and controlled experiments further reveal that the oxygen-substituted sulfur defects and the nearly exponential dependence of their concentrations on the temperature of WS₂ are the origin of the sharp PL enhancement. Our findings shed new light on the relationship between macroscopic PL property and atomic-level structures of monolayer TMDCs, which will benefit their optical related applications.

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Author contributions Liu B, Lin J, and Luo G conceived the project. Liu B, Lin J, and Luo G supervised the study. Zhao S prepared the samples with the help of Lai Y. Tan J and Lin J did the STEM measurements. Zhao S and Feng S performed the optical measurements. Ke C and Luo G performed the theoretical analysis. Ding B helped with data analysis. All authors discussed the results and wrote the manuscript.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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单层过渡金属硫族化合物中氧取代激活的光致发光增强

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摘要 具有原子层厚度的过渡金属硫族化合物(TMDCs)是一种适用于光子和光电子领域的新颖的半导体材料, 而增强其光致发光(PL)特性对于这类材料的光学应用至关重要. 尽管研究人员做了大量的工作来增强单层TMDCs的PL特性, 但微观结构和PL效率之间的复杂关系阻碍了对其性质的调控. 本文中, 我们证实了在激光辐照下, 单层TMDC的PL强度在经过一个预激活的平台后可以增强近一个数量级且半峰宽变窄约20%. 实验和理论研究表明, 低功率的激光辐照能够在WS₂中产生许多硫空位簇, 这些硫空位簇随后被氧取代并显著增强其PL. 这种PL增强的现象在其他单层TMDC材料中有普适性, 有利于TMDC在光学领域的应用.