

Formation of Brightly Luminescent MoS₂ Nanoislands from Multilayer Flakes via Plasma Treatment and Laser Exposure

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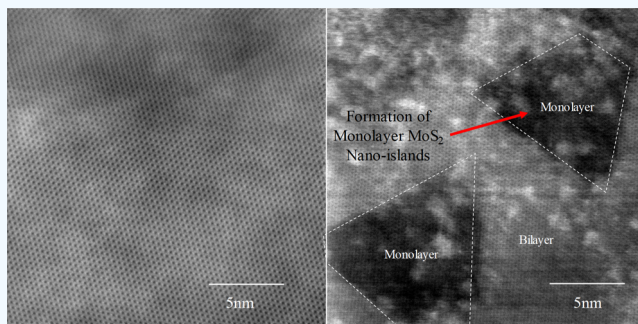


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Supporting Information

ABSTRACT: A robust and reliable method for enhancing the photoluminescence (PL) of multilayer MoS₂ is demonstrated using an oxygen plasma treatment process followed by laser exposure. Here, the plasma and laser treatments result in an indirect-to-direct band gap transition. The oxygen plasma creates a slight decoupling of the layers and converts some of the MoS₂ to MoO₃. Subsequent laser irradiation further oxidizes the MoS₂ to MoO₃, as confirmed via X-ray photoelectron spectroscopy, and results in localized regions of brightly luminescent MoS₂ monolayer triangular islands as seen in high-resolution transmission electron microscopy images. The PL lifetimes are found to decrease from 494 to 190 ps after plasma and laser treatment, reflecting the smaller size of the MoS₂ grains/regions. Atomic force microscopic imaging shows a 2 nm increase in thickness of the laser-irradiated regions, which provides further evidence of the MoS₂ being converted to MoO₃.



1. INTRODUCTION

Since 2010, intense research in the optical and optoelectronic properties of two-dimensional (2D) transition metal dichalcogenides (TMDCs) has led to great advancements in the materials preparation,^{1–9} processing,^{10–13} and devices.^{10,14–19} Many interesting physical phenomena are seen in these 2D materials, including lasing from monolayer MoS₂ deposited in photonic crystal cavities^{20,21} and interlayer excitons bound at the interface between WSe₂ and MoSe₂.^{22–26} While this intriguing class of materials presents new degrees of freedom in the design and optimization of optoelectronic devices, their extremely high surface-to-volume ratio makes them particularly sensitive to defects, surface contaminants, and other extraneous perturbations from the underlying substrate and environment.^{27–29} As such, post processing techniques are needed to mitigate these potential problems and, in general, provide a more robust material platform for reliable device fabrication.

Several techniques have been developed to treat MoS₂ flakes in order to increase their photoluminescence (PL) efficiency. Amani et al. reported that treatment with an organic superacid can uniformly enhance the PL and minority carrier lifetime of monolayer MoS₂ flakes with “near unity” quantum efficiency.¹⁸ Mouri et al. reported that chemical-doped monolayer MoS₂ flakes can show tunable and enhanced PL by changing the doping level of the doped MoS₂ flakes.³⁰ Our group reported both oxygen plasma-based and proton irradiation-based treatment of multilayer MoS₂ flakes that show stable direct band gap transitions and significantly enhanced PL efficien-

cies.^{8,27,28} In 2016, we reported that the PL intensity from multilayer MoSe₂ flakes can be enhanced through selective oxidation of one MoS₂ layer.³¹ Nan et al. reported substantial enhancements in the PL intensity from monolayer MoS₂ via chemical adsorption of oxygen at defect sites and high-temperature annealing, which provides an efficient mechanism for converting trions to radiative excitons.³² Kang et al. reported PL quenching in single-layer MoS₂ via oxygen plasma treatment.³³

While previous studies have investigated the effects of plasma treatment and chemisorption, here, we combine an oxygen plasma treatment with subsequent laser exposure to achieve a new state of the material system that is not achievable with the plasma alone or the laser alone. Using high-resolution transmission electron microscopy (HRTEM), we observe the emergence of triangular regions of monolayer MoS₂ (i.e., nanoislands) in the two-step process, which are highly luminescent. This approach enables patterning of specific regions of the TMDC material by the selective exposure to light. Several control experiments are carried out to understand the role of each step of the treatment (i.e., O₂

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plasma vs laser exposure) in the MoS₂-to-MoO₃ transformation.

2. RESULTS AND DISCUSSION

In the sample preparation process, crystalline MoS₂ is first mechanically exfoliated onto transparent polydimethylsiloxane. Based on the indirect band peak from PL spectra, once an MoS₂ flake of the desired size and thickness is located via optical microscopy, the flake is transferred using a home-built contact aligner (i.e., dry transfer method) with a 50× objective lens onto a transmission electron microscopy (TEM)-compatible silicon nitride substrate.³⁴ The flakes are then treated with a remote oxygen plasma for 3 min using an XEI Evactron Soft Clean plasma cleaner, in which the plasma is generated from room air flowing past a 15 W RF source at 200 mTorr. The flake is placed 10 cm downstream from the oxygen plasma source. In this remote configuration, the radical species lose most of their kinetic energy but still remain chemically reactive. The flake is then exposed to laser irradiation in ambient air using a 532 nm CW laser focused through a 100× (0.86 NA) objective lens to a beam of approximately 1 μm size and intensity of 3.5 mW/μm². PL spectra were collected from these MoS₂ flakes before and after the plasma/laser treatment using an inVia micro-spectrometer (Renishaw, Inc.) using a 532 nm-wavelength laser with a power density of 0.03 mW/μm², which is 2 orders of magnitude weaker than the laser exposure treatment and, thus, does not change the material during the PL measurements. X-ray photoelectron spectroscopy (XPS) was performed using a 10 μm spot size on a ULVAC PHI VersaProbe III (Physical Electronics, East Chanhassen, MN, USA) with a monochromated Al Kα source on the MoS₂ flakes before the treatment, after plasma treatment, and after the plasma and laser treatment. Atomic force microscopy (AFM) images of the laser-exposed regions in the MoS₂ were taken using dimension ICON AFM (Bruker, Inc.). Time-resolved PL (TRPL) spectra were taken from the MoS₂ flakes before the treatment, after plasma treatment, and after the plasma and laser treatment and were carried out on a laser scanning confocal optical microscope using a 50 fs pulsed 405 nm diode laser with a pump power of <60 nW and repetition rate of 20 MHz. The TRPL spectra were detected using single-photon avalanche photodiodes (SPCM-AQR-14, PerkinElmer) connected to a HydraHarp 400 (PicoQuant) time-correlated single-photon counting system. To rule out laser-induced heating effects, we have included results in the [Supporting Information](#) taken from a MoS₂ flake that was thermally annealed in an argon environment at 500 °C for 1 h, immediately following the plasma treatment.

Figure 1a shows a TEM image of a suspended MoS₂ bilayer, which is treated by oxygen plasma only. In this TEM image, we are able to clearly see the atomic lattice structure, which is almost the same as an untreated bilayer MoS₂ flake. **Figure 1b** shows a TEM image of a suspended MoS₂ bilayer after plasma and laser treatment, showing the formation of triangular and trapezoidal nanoislands, which is indicated by the different contrast (i.e., the difference in energy loss of the electron beam) of the TEM images, in this two-step process (i.e., plasma followed by laser exposure). Here, the nanoislands of the monolayer material are embedded within the bilayer MoS₂, indicating the partial conversion of one of the MoS₂ layers to MoO₃, which is consistent with the XPS data described below. It is also apparent from these images that the light-induced oxidation of the MoS₂ material follows the axes of the crystal,

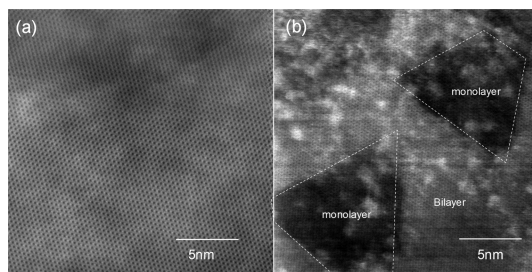


Figure 1. TEM images of MoS₂: (a) oxygen plasma-treated only and (b) oxygen plasma-treated and laser-exposed.

forming triangular patterns. These resulting monolayer nanoislands of MoS₂ are more than 1 order of magnitude more luminescent than the original bilayer material.

Figure 2a shows the PL spectra of bilayer MoS₂ (indicated by the position of the indirect band gap emission) taken before

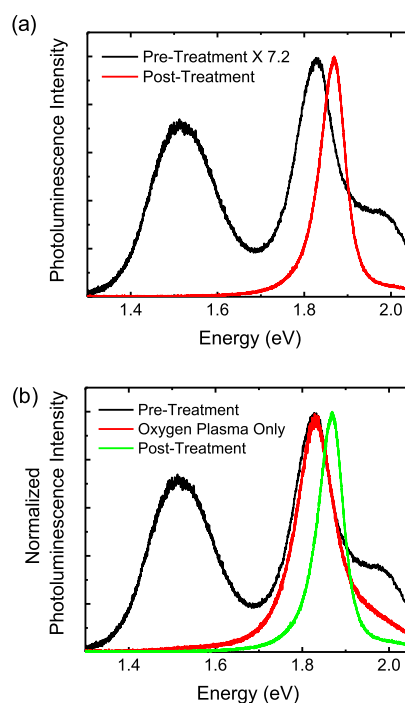


Figure 2. (a) PL spectra for a bilayer MoS₂ flake before and after plasma treatment and laser exposure. (b) Normalized PL spectra for the same bilayer MoS₂ flake taken before treatment, after oxygen plasma treatment only, and after oxygen plasma treatment and laser exposure.

and after plasma and laser exposure. Here, we see a 7.2-fold increase in the peak PL intensity after the treatment with a 22% linewidth narrowing and complete suppression of the indirect band gap transition. **Figure 2b** shows the PL spectra taken before treatment, after a 3 min oxygen plasma exposure only, and after a 3 min oxygen plasma and a 3 min laser exposure. Here, the effect of the laser exposure is to increase the energy (i.e., 40 meV blue shift from 1.83 to 1.87 eV) of the direct band gap emission, while the PL intensity remains unchanged. The laser exposure also produces a narrower distribution (98.5 to 65.5 meV) and a decreased lifetime of the ground-state exciton. As a control experiment, two few-layer MoS₂ flakes were thermally annealed at 500 °C in argon gas at a flow rate at 1 SLM after the plasma treatment step instead of

laser exposure. These results are shown in Figure S1 of the Supporting Information. We find PL intensity to be an order of magnitude weaker after thermally annealed flakes, indicating that the transition to MoO₃ with MoS₂ islands is a photodriven rather than thermally driven process with oxygen plasma-treated MoS₂ flakes.

Figure 3 shows XPS spectra of a 10 μm diameter region of multilayer MoS₂ flakes taken before and after plasma and laser

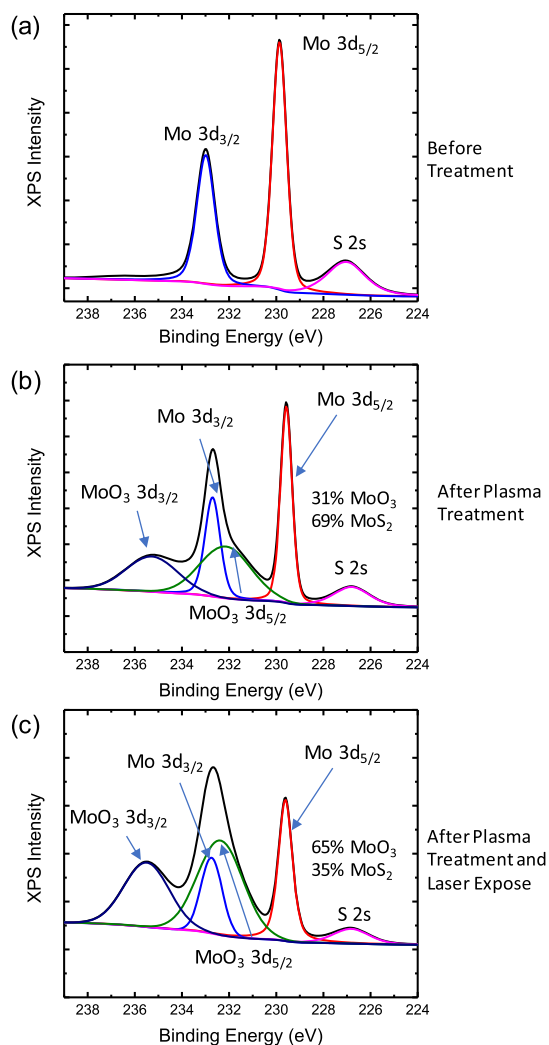


Figure 3. XPS spectra for (a) untreated, (b) oxygen plasma-treated only, and (c) oxygen plasma-treated and laser-exposed bilayer MoS₂ flakes.

exposures. Figure 3a shows the Mo 3d spectrum taken before treatment, where we observe Mo 3d_{3/2}, Mo 3d_{5/2}, and S 2s states that are consistent with stoichiometric MoS₂.³⁵ After oxygen plasma treatment, we observe two additional peaks that correspond to the MoO₃ doublet (i.e., MoO₃ 3d_{3/2} and MoO₃ 3d_{5/2} states), as indicated in Figure 2b.^{35–38} Based on these spectra, we believe that we have created subregions of MoO₃ within the MoS₂. Figure 3c shows the Mo 3d spectrum taken after oxygen plasma and a 60 s laser exposure. The MoO₃ contribution becomes more prominent, increasing from 31% of the total Mo 3d_{5/2} counts in Figure 2b to 65% in Figure 3c, indicating an additional transformation of MoS₂ to MoO₃.

Figure S2 of the Supporting Information shows optical microscopy and AFM images of a few-layered MoS₂ flake after

plasma treatment and laser exposure, showing an increase in thickness of 2 nm in the region that had undergone laser exposure. This increase in thickness is consistent with the formation of MoO₃, which has a larger thickness than MoS₂.^{39,40}

Figure 4 shows the result of PL lifetime measurements taken from treated and untreated MoS₂ flakes with the same

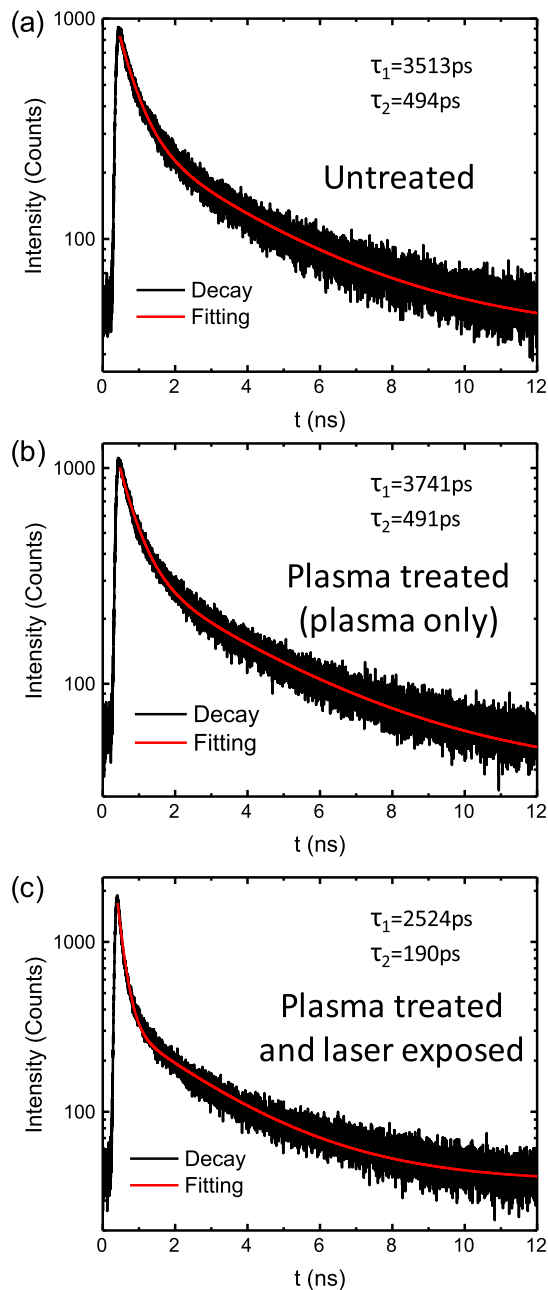


Figure 4. TRPL intensity for (a) untreated, (b) oxygen plasma-treated only, and (c) oxygen plasma-treated and laser-exposed MoS₂ flakes.

thickness (i.e., number of layers). Here, the PL lifetime decreases after oxygen plasma treatment and laser exposure. The time-dependent PL intensities were fitted to biexponential decays, as indicated in the figure. The first decay decreases from 494 ps before treatment to 190 ps after treatment. Here, the plasma-only treatment shows almost no effect on the PL

lifetime. We believe that the formation of small triangular regions of monolayer MoS₂ is primarily responsible for the shortened lifetimes because of the increased surface-to-volume ratio (or more accurately, the perimeter-to-area ratio), that is, nonradiative recombination occurring at the edges of each MoS₂ grain is primarily responsible for the decrease in the PL lifetime.

3. CONCLUSIONS

In conclusion, we report a two-step method for creating “triangular” MoS₂ nano-islands from exfoliated multilayer MoS₂ flakes using a sequence of plasma and light exposure treatments as observed in TEM images. This plasma/laser treatment induces a transition from indirect to direct band gap material, yielding a sevenfold enhancement in the direct band gap emission (at 1.87 eV) and suppression of the indirect emission (around 1.54 eV). Here, a slight spatial decoupling of the layers is created by intercalated O-species from the plasma treatment. The laser subsequently oxidizes exposed regions of the MoS₂ to MoO₃, as confirmed via XPS, which results in localized areas with brightly luminescent monolayer MoS₂ triangular nanoislands embedded in bilayer MoS₂. A 40 meV blue shift is also observed in the direct-gap emission with a 3 min laser exposure with a 33 meV decrease in the linewidth. Furthermore, we observe a decrease in the PL lifetime from 494 to 190 ps after the plasma and laser treatment, suggesting an increased density of monolayer MoS₂ grain boundaries. An increase in flake thickness is observed in the laser-irradiated regions, providing more evidence that the MoS₂ is partially being converted into MoO₃.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.0c02753>.

Optical and AFM images, PL spectra, and TEM images taken from multilayer MoS₂ flakes after oxygen plasma and thermal annealing (PDF)

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Notes

The authors declare no competing financial interest.

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