

# Microencryption on Atomic Monolayers Enabled by Direct Laser Writing

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**Abstract**—Tungsten disulfide ( $\text{WS}_2$ ), a 2D transition metal dichalcogenide, exhibits different chemical and physical properties in both its monolayer and bulk layer crystal forms. As  $\text{WS}_2$  monolayer flakes exhibit direct band gaps, they fluoresce when excited by light. They show strong edge fluorescence, as well as weak non-edge fluorescence that comes in a variety of distinct patterns and intensity. In contrast, such fluorescence is not present in bulk layer flakes. This project investigates the utilization of a focused laser beam to exfoliate  $\text{WS}_2$  bulk layer flakes into thinner monolayers that also show strong fluorescence comparable to that of monolayer flakes. In addition, we examine how a laser beam can modify monolayer flakes to increase their natural non-edge fluorescence intensity. Interestingly, when flakes are modified under deprivation of oxygen, such changes are no longer observable, implying that oxygen is responsible for the modification of fluorescence as well as the exfoliation of bulk layer flakes. A redshift in photoluminescence peak wavelength and changes in the surface height and phase of modified monolayer flakes also support the theory that oxidation is responsible for laser modification.

## I. BACKGROUND AND PURPOSE

Semiconductors conduct electricity under certain conditions. Their conductivity is dependent on the structure of their crystal lattice. One group of semiconductors is 2D transition metal dichalcogenides. They are of the form  $\text{MX}_2$ , where M and X represent the transition metal and chalcogen respectively. [1]

In tungsten disulfide ( $\text{WS}_2$ ), tungsten (W) and sulfur (S) atoms are situated in a trigonal prismatic coordination sphere where strong covalent bonds exist between W and S atoms, as shown in Figures 1i and 1ii.  $\text{WS}_2$  exists as either monolayer flakes (monoflakes) or bulk layers. The difference lies in their relative thicknesses. Monoflakes are atomically thin, whereas bulk layers flakes comprise multiple layers held together by weak van der Waals forces between successive  $\text{WS}_2$  layers, as shown in Figure 1iii. [1] [3] Monoflakes also lack an inversion centre and have direct band gaps, unlike bulk layer flakes which have indirect band gaps, as shown in Figure 1iv. [4] [5] These differences lead to different physical properties. Research regarding  $\text{WS}_2$  is of interest because of emerging applications in optoelectronics due to their interaction with light, as well as applications in field effect transistors (FETs) [6] [7] and in flexible semiconductors. [8]

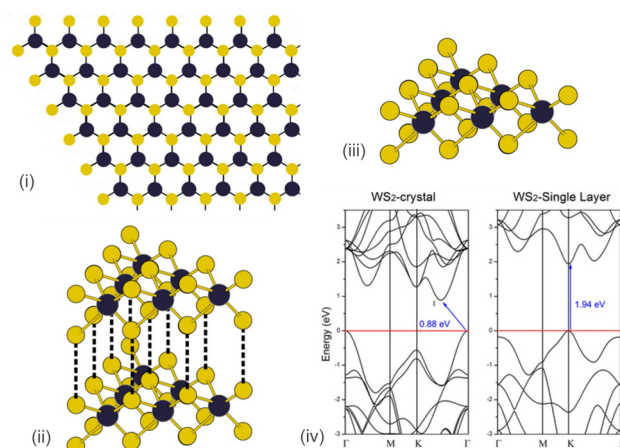


Figure 1. (i) top-down view of  $\text{WS}_2$  crystal structure (ii) iso-3D view of  $\text{WS}_2$  monolayer (iii) iso-3D view of van der Waals forces between consecutive layers in bulk layer crystals (iv) band gap nature of  $\text{WS}_2$  bulk layer and monoflakes [2]

Monoflakes have direct band gaps, and have much more potential applications in such fields due to their greater sensitivity to photons. In this project, we develop a novel method to synthesize  $\text{WS}_2$  monoflakes on demand and improve their properties using a focused laser beam. In addition, we carried out localized modification and determined that oxygen plays a role in this modification.

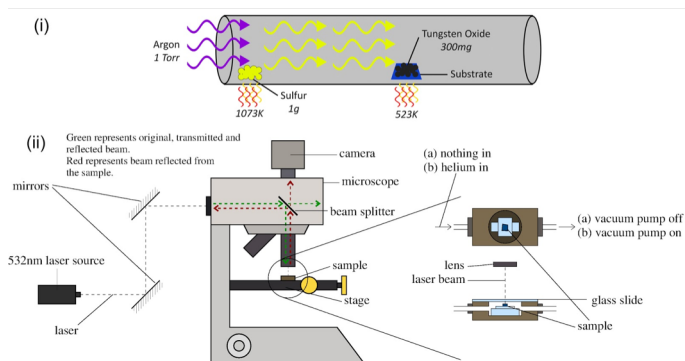


Figure 2. (i) chemical vapour deposition synthesis of  $\text{WS}_2$  flakes (ii) laser modification setup

## II. METHODOLOGY

WS<sub>2</sub> flakes were synthesized using chemical vapor deposition, as shown in Figure 2i. We placed 300 mg of tungsten oxide powder in the centre of a tube furnace and placed 1 g of sulfur powder upstream which was controlled by an additional heating source. During growth, the temperature of the furnace was ramped to 800°C at a rate of 30°C/min while the sulfur was heated separately to 250°C. The source vapor was carried by argon gas at a constant flow rate of 50 cm<sup>3</sup>/min. Pressure and temperature were maintained at 1 Torr and 800°C for 15 min before cooling to room temperature.

A fluorescence microscope (FM) with a mercury light source was used to observe fluorescence of the synthesized flakes. It also has a lower intensity xenon light source for capturing bright field images. The fluorescence of WS<sub>2</sub> flakes can be observed under specific ranges of excitation wavelengths including yellow light (545 - 580 nm).

A standard optical microscope, together with a 532 nm laser, was used for laser modification of WS<sub>2</sub> as shown in Figure 2ii. The focused laser beam remained fixed while the sample was moved using computerized stage controls to achieve focused scanning.

To achieve an oxygen deprived environment, the WS<sub>2</sub> sample was first placed in a container with a glass slide lid, as shown in Figure 2ii. An air pump was used to remove air until the internal pressure reached 0.08 Torr. Helium gas was then pumped in till a constant pressure of 0.8 Torr was achieved for 30 minutes. This process was then repeated.

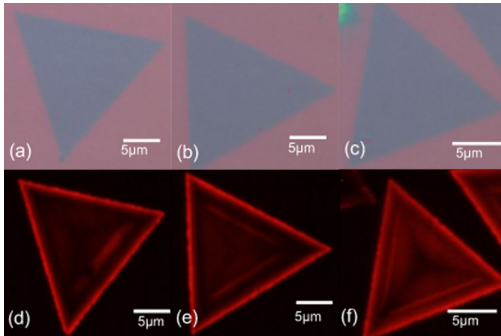


Figure 3. (a)-(c) as grown monolayer flakes under optical microscope (d)-(f) as grown monolayer flakes under fluorescence microscope

## III. SYNTHESIZED FLAKES

Monoflakes have a distinct light blue color under an optical microscope (OM) and exhibit fluorescence under yellow light, as shown in Figure 3. The edges have significantly stronger fluorescence, possibly due to higher sulfur to tungsten ratio along the edge, resulting in more free electrons available to be promoted when excited by photons. Hence, more excitons are formed and more photons are emitted, leading to more intense fluorescence. [10]

Non-edge fluorescence patterns of monoflakes are due to the heterogeneity of WS<sub>2</sub> crystals. Chemical vapor deposition results in the creation of regions with different W:S ratios [11] which in turn gives rise to different fluorescence intensities.

Bulk layer flakes come in varying thicknesses. Under OM, thin flakes appear dark green while thicker flakes appear yellow. Under yellow light excitation, no bulk layer flakes exhibit fluorescence like monoflakes do. The spots of fluorescence seen in Figure 4i are due to the presence of exposed thin layers. In WS<sub>2</sub> monoflakes, due to the direct band gap, photons are readily absorbed, promoting electrons to the conduction band. [4] [5] However, bulk layer WS<sub>2</sub> crystals have indirect band gaps, so electrons must also undergo a shift in crystal momentum to jump to the conduction band. Thus, photons are not readily absorbed and emitted [12] and bulk layer flakes do not fluoresce.

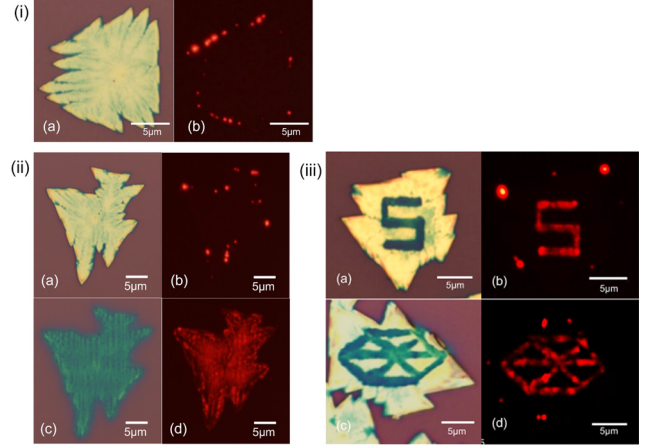


Figure 4. (i) as grown bulk layer flake under OM (a) and yellow light (b), (ii) laser exfoliation of bulk layer flake before under OM (a) and yellow light (b), and after under OM (c) and yellow light (d), (iii) selective exfoliation of bulk layer flake under OM (a) (c) and yellow light (b) (d)

## IV. EXFOLIATION OF BULK LAYER FLAKES

As bulk layer flakes are exfoliated with a laser beam, their thickness decreases and their fluorescence drastically improves as they become a monoflake, as shown in Figure 4ii. This exfoliation was performed with a 70 mW laser, and the flake scanned twice with scanning speed 20 μm/s. This confirms our hypothesis that a laser can be used for both exfoliation and improvement of fluorescence of bulk layer flakes.

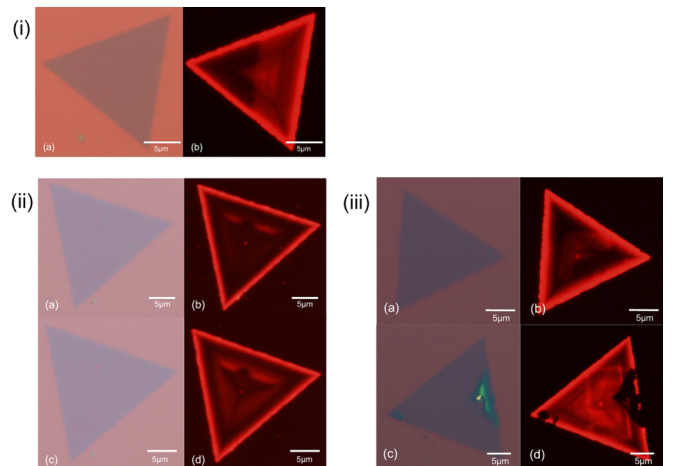


Figure 5. (i) right half modified monolayer flake under OM (a) and FM (b), (ii) laser modification of monolayer flake before under OM (a) and FM (b), (iii) laser modification of monolayer flake after under OM (a) and FM (b)

and after under OM (c) and FM (d), (iii) selective modification of monolayer flake under OM (a) (c) and FM (b) (d)

In addition, exfoliation of bulk layer flakes only occur to areas directly exposed to the laser, as compared to conventional chemical and physical methods of exfoliation, which reduces the layers across the entire flake. Therefore, it is possible to scan the flake under the laser beam in a specific pattern to form the same pattern under OM and yellow light, as shown in Figure 4iii.

## V. MODIFICATION OF MONOLAYER FLAKES

The fluorescence of WS<sub>2</sub> monoflakes too can be modified using the focused laser beam. A distinct improvement in fluorescence can be observed at regions subjected to the laser beam, as shown in Figures 5i & 5ii. This modification was performed with a 35 mW laser beam, and the flake is rastered twice with scanning speed 20 μm/s. The contrast between modified and pristine regions show that laser modification can improve the fluorescence and optical properties of monoflakes. At higher powers, fluorescence can be deprived as the flake deteriorates.

Similar to exfoliation of bulk layer, This method only modifies the regions directly in contact with the laser beam as compared to chemical methods, which would modify the entire sample. Thus, drawing a pattern on a monoflake will produce a similar fluorescence pattern. This is possible for both high and low power modification, where fluorescence is decreased or increased respectively, as seen in Figure 5iii.

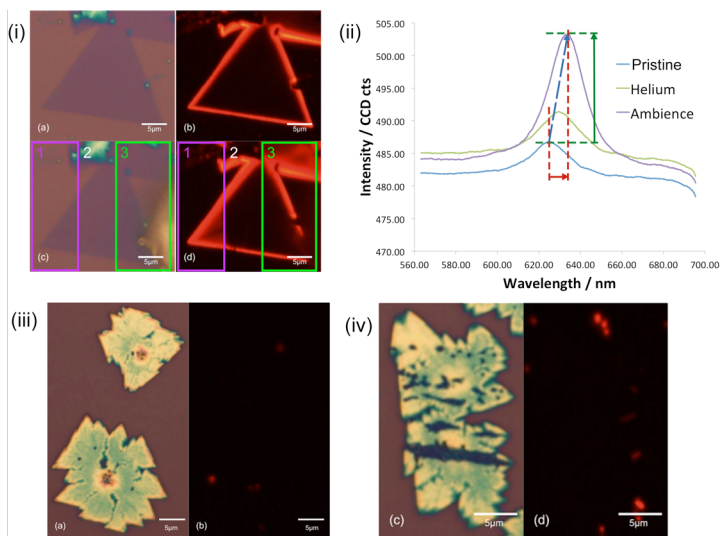


Figure 6. (i) laser modification of monolayer flake before under OM (a) and yellow light (b), and after under OM (c) and yellow light (d), region 1 in ambience, region 2 left pristine, region 3 in helium, (ii) photoluminescence analysis of pristine, helium modified, and ambience modified monolayer, (iii) low power exfoliation of bulk layer flake in helium environment, (iv) high power exfoliation of bulk layer flake in helium environment

## VI. ANALYSIS OF MODIFICATION

In this section, we investigate the mechanism behind laser modification. Considering that laser heating is occurring in an ambient environment, we hypothesize that oxygen is responsible for both laser modification and exfoliation of WS<sub>2</sub> flakes. To verify this, the following experiment was conducted. Two regions (1 and 3) of a monoflake were modified in ambience and

helium respectively while a third (2) was left unmodified. The fluorescence images of the flake and photoluminescence spectra (PL spectra) at points in each region are presented in Figure 6i and 6ii. There is an increase in peak intensity and a redshift, showing that the region modified in ambience displays a significant concentration of a different chemical species.

The above observation holds for bulk layer flakes too. When a bulk layer flake was modified in helium under the same parameters as in ambience, there was no visible exfoliation or fluorescence (Figure 6iii). Only when the laser beam was set to an extremely high power in absence of oxygen was there a definite reduction in the number of crystal layers. Even then, no fluorescence was exhibited (Figure 6iv). This result serves as evidence for the co-existence laser sublimation-oxidation theory, suggesting that oxidation of WS<sub>2</sub> allows sublimation of other layers at a lower activation energy.

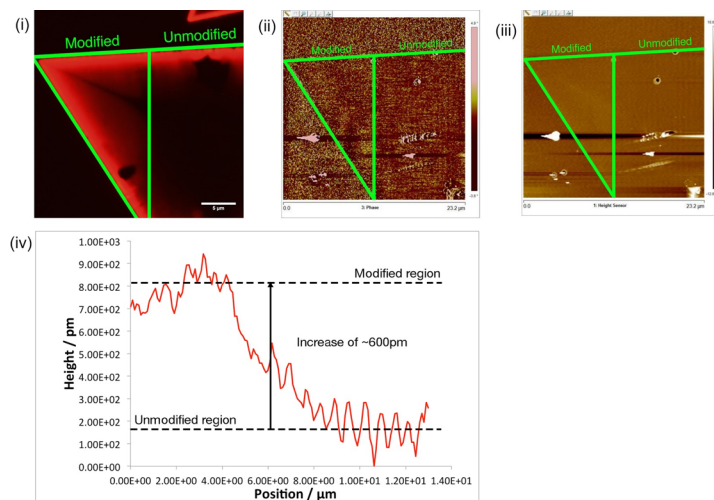


Figure 7. (i) fluorescence of corner modified monolayer flake under yellow light, (ii) phase profile of corner modified monolayer flake, (iii) height profile of corner modified monolayer flake, (iv) height graph of corner modified monolayer flake

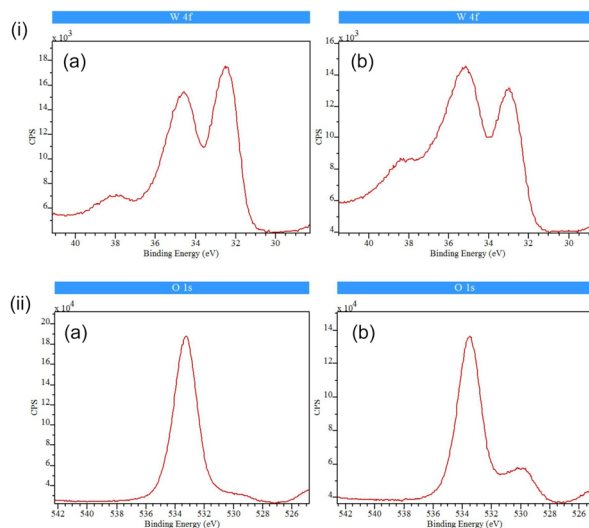


Figure 8. (i) XPS analysis of monolayer tungsten atoms before laser modification (a) and after (b), (ii) XPS analysis of monolayer oxygen atoms before laser modification (a) and after (b)

The phase and height profile of a selectively modified monoflake can be seen under the atomic force microscope, as shown in Figure 7i to 7iii. There is a difference between the modified and unmodified regions of the flake in the phase profile, indicating a chemical change. The height profile picture shows that the flake is generally uniform, but Figure 7iv shows us that the modified region is thicker than the unmodified region by about 0.6 nm, possibly due to addition of oxygen during laser modification.

Through X-ray Photoelectron Spectroscopy (XPS), the ratio of the elements present in the monoflake can be found. By comparing the intensities of the different peaks for a monoflake before and after modification, it can be inferred that there is a change in binding energies of the 4f<sub>5/2</sub> and 4f<sub>7/2</sub> peaks for W and the 1s peak for O. This implies that the compound's new chemical composition is WO<sub>x</sub>S<sub>2-x</sub>, the exact formula of which can be found after the further quantitative analysis is performed on XPS results.

## VII. CONCLUSION

Since a significant increase in fluorescence intensity is observed only when WS<sub>2</sub> monoflakes and bulk layer flakes were modified in ambient, it can be deduced that oxygen is involved. The peak shifts in PL and the phase profile in AFM strongly support the involvement of a chemical process. The evidence that the process is the incorporation of oxygen into the WS<sub>2</sub> crystal structure to form WO<sub>x</sub>S<sub>2-x</sub> is given by XPS. This WO<sub>x</sub>S<sub>2-x</sub> formed through laser modification is observed to exhibit brighter fluorescence than WS<sub>2</sub> under excitation by yellow light. Unfortunately, there are no previous studies that can be used to confirm our observations as none demonstrated that the impure form, WO<sub>x</sub>S<sub>2-x</sub>, fluoresces under yellow light.

The physical reduction in number of layers of bulk layer crystals during bulk layer exfoliation is due to heating of the layers resulting in sublimation. [14] However, when deprived of oxygen, a significantly higher laser power is required. This suggests that oxygen is required for exfoliation and that in addition to sublimation, oxidation is taking place.

## VIII. APPLICATIONS

Our experiments have allowed us to develop a greater understanding of the chemical processes that take place when a flake is excited by a laser beam. Firstly, we have demonstrated that on demand exfoliation of bulk layer flakes into monoflakes is possible under a laser beam, allowing synthesis of large areas of WS<sub>2</sub> monoflakes. Due to the localized nature of laser exfoliation as compared to chemical or mechanical exfoliation, micropatterning can also be performed, by selectively exfoliating specific regions of the WS<sub>2</sub> bulk layer flake rather than the entire flake. In addition, laser modification can tune the optical properties and fluorescence on monoflakes. This modification does not cause any visible optical change, which

means it is possible to “encrypt” information that can only be observed as fluorescence under yellow light.

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