Second-harmonic generation enhancement by defects-level control in monolayer tungsten disulfide

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Lateral homojunctions in as-grown CVD monolayer WS_2 have been recently reported by H. Liu and collaborators [1]. These homojunctions, as observed by fluorescence microscopy, may give rise to photoluminescent (PL) concentric patterns of alternating bright and dark regions. Further EDX analysis and DFT calculation revealed this phenomenon is due to chemical heterogeneity, as bright PL areas have less sulfur (S) vacancies (thus PL emission is dominated by excitons) and dark PL areas have more S vacancies (thus increasing the density of mid-gap-states).
These results may impact on the nonlinear optical properties of monolayer WS_2 crystals, since the second-order susceptibility of the material may experience an improvement in the infrared due to the presence of the mid-gap-states. To test this hypothesis, we have performed second harmonic generation (SHG) mapping at 1550 nm in monolayer WS_2. The experimental setup for SHG is identical to [2].
As shown in Figure 1, in a triangular WS_2 flake, PL emission is stronger at the borders of the flake, while similar edge effect is not observed in SHG. In fact, PL and SHG in these flakes are anticorrelated and determined by the electronic band structure of the material – although not occurring simultaneously. SHG is stronger in the internal region of the crystal, where mid-gap-states may be responsible for the quasi-resonant second-order nonlinear effect.
We also observed that, after 2 months of exposure to environmental conditions, both PL and SHG signals decrease dramatically. In fact, if the S vacancies are filled up by oxygen, our DFT calculations show that the bandgap of the material can turn from direct to indirect, causing the excitonic and mid-gap-states to disappear.
Finally, we can conclude that SHG at 1550 nm in monolayer WS_2 is highly dependent on the defect level (S vacancies) of the material. This result may lead to potential second-order optical nonlinearities enhancement in WS_2 and other TMDs in the infrared via defects level engineering.

References

[1] H. Liu *et al.*, Nano Letters, 16(9) (2016) 5559-5567
[2] M. J. L. F. Rodrigues *et al.*, Advanced Materials, 28(48) (2016) 10693-107000

Figures

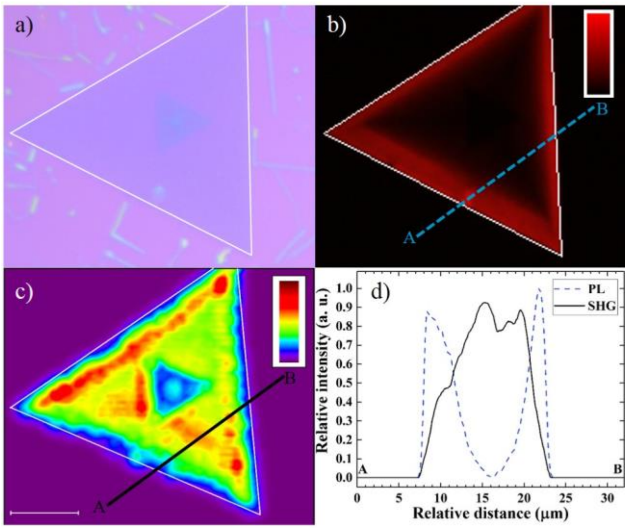

Figure 1: imaging characterization of WS_2 sample: a) optical image; b) fluorescence microscopy image; c) false-color SHG image; d) anticorrelation profile between PL and SHG. Scale bar = 10 µm.