NEAR-INFRARED EMISSION FROM SULFUR VACANCIES IN MoS2 MULTILAYER FLAKES

F. Fabbri1, E. Rotunno2, E. Cinquanta4, D. Kaplan6, L. Lazzarini3, M. Bernasconi5, C. Ferrari3, M. Longo4, A. Molle4, V. Swaminathan6 & G. Salviati3*

1 NANO-CNR Institute c/o Scuola Normale Superiore, Piazza San Silvestro 12 - 56127 Pisa, Italy
2. NANO-CNR Institute and c/o UNIMORE Via Giuseppe Campi, 213, 41125 Modena MO
3 IMEM-CNR Institute, Parco Area delle Scienze 37/A, 43124 Parma, Italy
4 Laboratorio MDM, IMM-CNR, via C. Olivetti 2, I-20864 Agrate Brianza, Italy.
5 Dipartimento di Scienza dei Materiali, Universita` di Milano-Bicocca, Via R. Cozzi 55, 20126 Milano, Italy.
6 U.S. Army RDECOM-ARDEC, Fuze Precision Armaments and Technology Directorate, Picatinny, NJ 07806, USA.
**giancarlo.salviati@cnr.it*

We report on the experimental evidence, confirmed by ab-initio calculations, that sulfur vacancies give rise to a novel near-infrared emission at 0.75 eV in MoS2 flakes and that ripplocations redshift the MoS2 indirect bandgap emission.
Keywords: NIR-emission, S-vacancies

1. Introduction

One of the advantages of two-dimensional (2D) transition metal dichalcogenides (TMDs), e.g. with respect to graphene, comes from quantum confinement, enabling the indirect-to-direct bandgap transition as a function of the thickness [1]. This particular effect can lead to a strong interaction with light, envisioning the next generation of visible light-emitting devices. The analysis of the extended crystal defects, either intrinsic or extrinsic, in 2D nanoflakes is still in its early stage and deserves a dedicated approach to understand how novel electronic and/or optical properties can be engineered by controlling the nucleation of extended defects. In this respect, most of the consideration was devoted to the generation and/or the structural properties of crystal defects [2]. Structural defects in 2D TMDs, including point defects, ripplocations (line defects with a dual nature of surface ripple and crystallographic dislocation [3]) and grain boundaries, are scarcely considered regarding their potential to affect the optical properties of this class of materials. A focused analysis of crystal defects, either intrinsic or extrinsic, in 2D nanoflakes can clarify how novel optical properties can be engineered by controlling the nucleation of lattice defects.

2. Results

In this work we report on the experimental evidence of a near-infrared (NIR) emission from crystalline defects in MoS2 multilayer flakes exfoliated from bulk molybdenite. Cathodoluminescence (CL) spectroscopy and mapping reveal that the MoS2 flake's edges present an intense emission in the NIR range (peaked at about 0.75 eV) (Figure 1). According to electron energy loss spectroscopy and mapping (EELS) results and ab initio calculations of the defect-related intra-bandgap states energies, the origin of this emission is ascribed to the high concentration of sulfur vacancies (Vs) (Figure 2). High-resolution transmission electron microscopy (TEM) and Raman spectroscopy and mapping show the presence of ripplocations and assess the defective behaviour of the MoS2 flake's edges. In particular, the ripplocations induce a strong redshift and broadening of the indirect band-to-band transition of MoS2, peaked at 1.25 eV as evidenced by CL spectroscopy and mapping [4]. Despite the great attention devoted in the literature to MoS2 monolayers, we believe that our results will convince that MoS2 multilayer flakes can be considered good candidates for future technological applications, provided tailored defect engineering is achieved. Indeed, since the chalcogen vacancy has the lowest formation energy for all the 2D TMDCs, our findings have a general validity making the field of MX2 (M: metal; X: chalcogenide) flakes with thickness t >1 ML fertile for emerging optical technological applications with accurately tailored properties

3. Figures

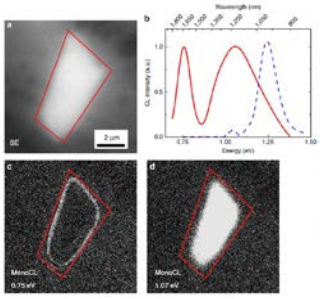

Fig. 1: (a) SEM image of the MoS2 flake. (b) CL spectrum of the MoS2 flake (solid line) and spectrum of molybdenite as a reference (dashed line). (c, d) Monochromatic CL maps at 0.75 eV and 1.07 eV.

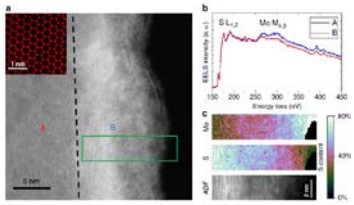

Fig. 2: (a) HAADF-STEM image of the edge of an exfoliated MoS2 flake and its atomic structure shown in the inset. (b) EELS spectra obtained in Two positions marked A and B in a) with the same number/colour code. (c) EELS spectrum images of the green rectangle in a.

References

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