Elena Blundo's PhD Thesis Summary

Dome-shaped two-dimensional crystals: A playground for the study of the crystal mechanical and optoelectronic properties

Due to the fascinating phenomena potentially associated with (quasi) two-dimensional (2D) systems, great interest for these systems started arising since the first half of the 20th century. The existence of truly 2D crystals in stable form was however predicted to be impossible due to a divergent contribution of thermal fluctuations [1, 2]. The possibility to explore a truly 2D world seemed, therefore, denied until the ground-breaking discovery of graphene. Graphene —a single layer of carbon atoms tightly packed into a 2D honeycomb lattice— was first isolated in 2004 by A. K. Geim and K. S. Novoselov neither with specific devices nor via ultra-complicated techniques, but via the simple —though brilliant— use of scotch tape to 'peel away' single layers of graphite [3]. The isolation and stability of graphene, previously thought to be impossible, opened the doors of Flatland [4] to the condensed matter physics community. Since then, the family of 2D systems has grown rapidly, as many other crystals have been found to be characterised by a layered structure akin to graphite, with different layers bound together by weak van der Waals (vdW) forces. Among them, graphene features a semi-metallic nature and is characterised by exceptionally high carrier mobilities; hexagonal boron nitride (hBN) is an extremely good insulator and dielectric with a large bandgap; black phosphorus (BP) possesses interesting properties that arise from its inherent in-plane anisotropy, and, as a consequence, from its anisotropic band structure; the family of transition metal dichalcogenides (TMDs, such as MoS_2, WS_2, $MoSe_2$, WSe_2, $MoTe_2$, WTe_2, NbS_2, $NbSe_2$, etc.) is richly varied, as it comprises some superconducting materials with charge density waves and Weyl semimetal properties, as well as many semiconducting materials, with bandgaps ranging from the visible to the near infrared spectral region. In the single layer limit, semiconducting TMDs (*e.g.*, MoS_2, WS_2, $MoSe_2$, WSe_2, and $MoTe_2$) are characterised by an extremely efficient light emission, which makes them ideal candidates for the realisation of innovative, flexible optoelectronic devices. Finally, post-transition-metal chalcogenides (MCs, such as InSe and GaSe) have recently attracted interest as 2D semiconductors, for their high carrier mobilities and their potentiality for hydrogen storage.

Aside from the possibility of exploring the effects of lower dimensionality on the properties of atomically thin crystals, the existence of these crystals in stable form opens new avenues to materials engineering. Indeed, the inherent all-surface nature of these systems entails a higher sensitivity to external perturbations [5, 6], which can in turn be exploited to modify the material properties. Among all possible external perturbations, the incredible mechanical flexibility and robustness [7, 8, 9] of 2D crystals offer the possibility to subject them to high mechanical deformations, engendering strains larger than 10 %. Such strains are able to induce major modifications in the electronic, optical, magnetic, transport and chemical properties of 2D materials, leading to the observation of a plethora of intriguing phenomena —ripe with new physics and novel opportunities.

In the past decade, great attention has been devoted to the development of methods to mechanically deform 2D crystals, that enabled the attainment of strain fields much larger than those generally achievable in conventional bulk semiconductors and quantum wells [10, 5], originating intriguing novel phenomena. Research in this field is hot and is paving the way towards the creation of planar electronic devices with ultralow-power consumption, flexible electronics, sensors, and components for energy scavenging and storage [5].

This thesis is focused on the development of an original strategy to induce strain fields in 2D crystals, and on the study of the effect of strain on the peculiar properties of the material.

The initial part of the Thesis aims at presenting the innovative method to induce strain in TMDs and hBN pioneered by the candidate and her group. This method is based on the irradiation of bulk flakes (*i.e.*, with thickness from tens to hundreds of nm) of these materials with low-energy (few eV) hydrogen ions. By using this approach, it is possible to induce —on the flake surface— the formation of domes with thickness of one-to-few layers and filled with pressurised hydrogen, as can be seen in Fig. 1. The domes were observed to form in many TMDs (MoS_2, $MoSe_2$, $MoTe_2$, WS_2, WSe_2, and WTe_2) [11] and in hBN [12], but not in other van der Waals crystals such as SnS_2 [13], InSe [14] and graphene-based samples [15, 16, 17, 18], where H atoms preferentially bind or interact with the crystal matrix rather than penetrating through it and remaining in the interlayer region.

TMD domes are particularly interesting since they are constituted by a single layer of the material [11, 19, 20] and feature a remarkable capability to emit light efficiently, even at room-temperature, as shown in Fig. 1(d). Indeed, such structures are highly deformed (or *strained*), which affects the properties of the material giving rise to novel effects. The properties of these domes, and in particular the role played by strain, are widely studied and discussed in the Thesis.

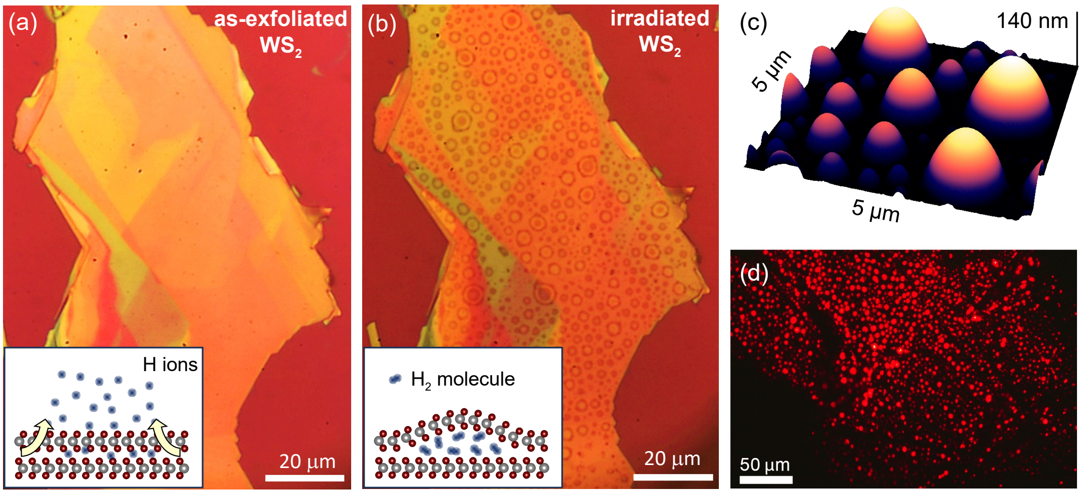

Figure 1: Optical image of a WS_2 flake before (a) and after (b) irradiation with H ions. The H dose was $d_H = 8 \times 10^{16}$ ions/cm^2. Insets: sketch of the H-ion irradiation process (a) and of the formation os a WS_2 dome filled with molecular hydrogen (b). (c) Atomic force microscopy image of a TMD flake treated with dose $d_H = 4 \times 10^{16}$ ions/cm^2, showing the presence of relatively large domes (diameter of a few μm); (d) Optical image of the red light emitted by a WS_2 flake with domes, at room-temperature. The image of the luminescence was obtained by exciting the flake with a green laser and detecting the PL signal with a CCD camera (the laser light was filtered out by a filter when acquiring the image). Panels (a)-(b)-(d) are reproduced from D. Tedeschi, E. Blundo *et al.*, Adv. Mater. **31**, 1903795 (2019) [11]. Copyright 2019 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. The insets of panels (a)-(b) are reproduced from E. Blundo *et al.*, Phys. Rev. Lett. **127**, 046101 (2021) [21]. Copyright 2021 American Physical Society.

First, an in-depth characterisation of the vibrational properties of the domes is presented, highlighting their link with the strain distribution. The Thesis discusses in particular Raman studies of TMD domes [21], and Raman and infrared (IR) characterisations of hBN domes [12]. These studies reveal huge shifts and splittings of the vibrational modes. The latter can be correlated with the strain magnitude and character, which is estimated via numerical calculations [11, 22, 23, 21].

Such numerical calculations provide an excellent means for estimating strain, but do not allow us to achieve an immediate understanding of the mechanical and elastic properties of the material. The candidate thus focused her research on the theoretical investigation of the morphology and mechanics of the system. In particular, the candidate developed an analytical method to describe the domes, which was coupled to morphological and mechanical experimental measurements performed through atomic force microscopy measurements [21, 24, 25, 26]. Such analytical method describes the shape and strain of domes with unprecedented accuracy, comparable to that obtained via numerical calculations, and allows one to obtain precious information on the elastic properties of the membrane and on the adhesion energy between the monolayer and the bulk crystal [21]. The Thesis describes in detail the analytical method and provides a survey of the elastic parameters and adhesion energy estimated through it for a variety of crystals. Such fundamental parameters are of key importance for the utilisation of 2D materials in flexible devices and for the creation of 2D heterostructures, where two or more 2D crystals are stacked together to create super-structures with novel properties. [27, 28].

The detailed knowledge of the strain status of the system opens the doors towards its exploitation to investigate the effect of strain on the optoelectronic properties of semiconducting TMDs.

The latter were probed through steady-state and time-resolved photoluminescence (PL) studies with sub-micron spatial resolution (μ-PL). Indeed, the PL signal of TMD mono- or few-layers is dominated by *free excitons*, *i.e.* electron-hole pairs bound by the Coulomb attraction. In TMD monolayers, the bandgap is direct, involving electrons and holes at the K point of the Brillouin zone. This results in a very efficient PL signal attributable to the direct exciton. The measurements performed by the candidate and discussed in this Thesis highlight the remarkable effect of strain on the PL emission, resulting in a sizeable energy shift of the direct exciton, and, for sufficiently high strains, in a peculiar direct-to-indirect exciton crossover [22]. This crossover is typically observed at the dome apex, see Fig. 2(a). Indeed, this deeply affects the emitted light intensity and decay time, as demonstrated by the candidate's studies [22].

Direct and indirect excitons in strained TMD monolayers were also investigated under the presence of high magnetic fields (such studies were performed by the candidate at the High Field Magnet Laboratory in the Netherlands). Indeed, magnetic fields induce a Zeeman splitting of the exciton energy in TMD monolayers, which is promising for their utilisation for valleytronics. The effect of strain on the Zeeman effect had however not been investigated so far. The candidate performed magneto-μ-PL experiments on the domes, as shown in Fig. 2(b), revealing an unexpected strain-induced decrease in the absolute value of the gyromagnetic factor (g_{exc}, where $\Delta\mathrm{E} = g_{\mathrm{exc}}\ \mu_{\mathrm{B}}B$, $\Delta\mathrm{E}$ being the Zeeman splitting and μ_{B} the Bohr magneton). The results presented in this Thesis shed light on this yet unexplored field, and highlight an unexpected behaviour, that unveils hybridisation phenomena between nearly resonant direct and indirect excitons [29].

Finally, more application-oriented studies of the system were performed. First, this Thesis demonstrates the possibility to engineer the domes. Lithography-based approaches were in fact used to pattern the flakes prior to irradiation, in order to achieve control over the size and position of the domes, see Fig. 2(c) [11, 30].

The unique possibility to create ordered arrays of light-emitting domes was further explored towards the generation of quantum emission. Indeed, several studies showed how quantum emitters are typically achieved in strained WSe_2 monolayers at cryogenic temperatures [31]. Quantum emitters were also observed by the candidate in monolayers of the alloy WSSe [32]. Since the domes host remarkable strain, they would be ideal candidates. However, due to the fact that they contain molecular hydrogen, the domes deflate at cryogenic temperature (below about 32 K hydrogen turns from gas to liquid). The candidate and her group developed a strategy to prevent the dome deflation process at cryogenic temperatures, based on a capping process of the domes (hBN thin flakes are deposited over the domes) [33]. This allowed us to observe narrow lines associated to quantum emission in the PL spectra of WS_2 domes at cryogenic temperatures, see Fig. 2(d)-(e). This represents the first non-electrical generation of quantum emitters in WS_2 monolayers, thus opening the doors towards its utilisation for quantum applications [33].

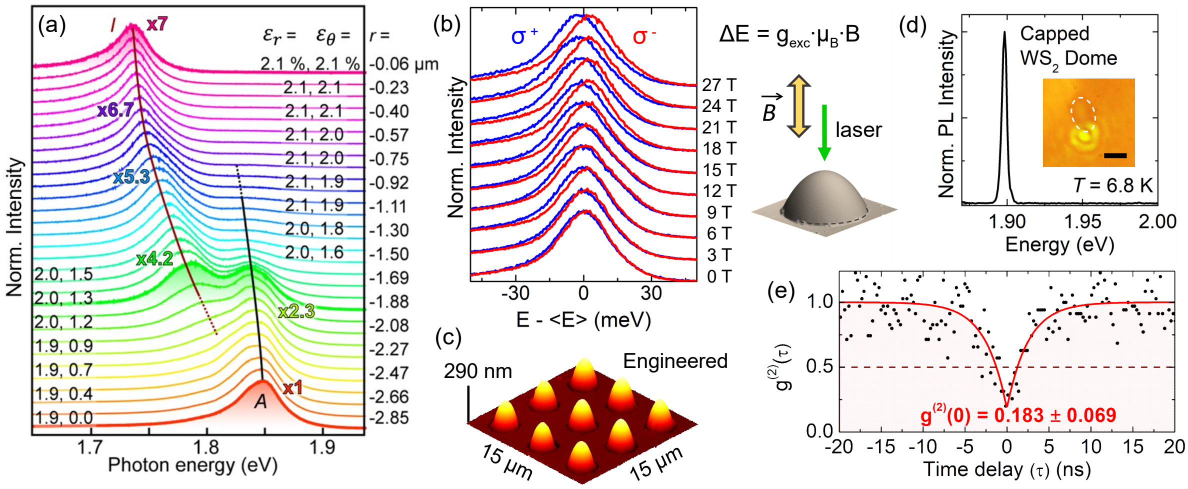

Figure 2: (a) Evolution of the normalised μ-PL spectrum of a WS_2 dome, as the laser spot is scanned from the dome left edge (bottom) to its apex (top). The spectra were acquired at room-temperature. Some spectra are labelled with the position of the laser spot (r) and with the values of the radial (ε_r) and circumferential (ε_θ) components of the strain tensor. The solid lines follow the energy shift of the peaks associated with the A (black line) and I (wine line) exciton transition. Reproduced from E. Blundo *et al.*, Phys. Rev. Res. **2**, 012024(R) (2020) [22]. Copyright 2020 The Author(s). (b) Left: Room-temperature normalised magneto-μ-PL spectra of a WS_2 dome filtered by circular polarisation $\sigma^{\pm}$. The spectra were acquired by keeping the sample in a bitter magnet and increasing the magnetic field from 0 to 27 T. The spectra are stacked by y-offset for ease of visualisation. At each field, the average energy between the σ^+ and σ^- components was subtracted from the absolute energy scale for ease of comparison. Top-right: Equation that links the exciton gyromagnetic factor (g_{exc}) to the Zeeman splitting (ΔE, *i.e* the energy difference between the σ^+ and σ^- components), where μ_{B} is the Bohr magneton. For this dome, $g_{\mathrm{exc}} = -2.47 \pm 0.10$ (while in unstrained monolayers $g_{\mathrm{exc}} \approx -4$). Bottom-right: Sketch of the experiment, in which the applied magnetic field is perpendicular to the dome surface, and the laser spot that excites the PL signal is focused at the dome centre. Reproduced from E. Blundo *et al.*, Phys. Rev. Lett. **129**, 067402 (2022) [29]. Copyright 2022 The Author(s). (c) 3D atomic force microscopy image of an ordered array of MoS_2 domes obtained by a lithography-based approach. Reproduced from E. Blundo *et al.*, Adv. Mater. Interfaces **7**, 2000621 (2020) [30]. Copyright 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (d) μ-PL spectrum of a WS_2 dome capped with hBN at a temperature of 6.8 K. Laser power: 20 μW. The inset shows an optical image of the dome and its area excited by the laser at 6.8 K. The white dashed line highlights the dome asymmetric profile. Scalebar: 2 μm. (e) Second-order autocorrelation function $g^{(2)}(\tau)$ measured for the emitter of panel (d). Panels (d)-(e) adapted from S. Cianci, E. Blundo *et al.*, Adv. Opt. Mater. **11**, 2202953 (2023) [33]. Copyright 2023 The Authors.

In the final part of her Thesis work, the candidate investigated a novel perspective: that of exploiting selective strain engineering in van der Waals heterostructures. Specifically, the candidate focused on the creation and study of novel heterostructures made of a TMD dome and of an InSe unstrained layer. Our studies revealed how strain is able to modify the electronic properties of the heterostructure, enabling an incredibly strain-activated efficient carrier tunnelling from the strained TMD monolayer to the InSe one [34]. Such new and original studies represent an important step in the hot field of 2D heterostructures, opening new perspectives related to strain engineering.

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