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Microphotoluminescence (μ PL) measurements of bidimensional materials in a custom-made setup

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Abstract. The continuously growing interest in the so called bidimensional (2D) materials has been accompanied by a parallel development of techniques specifically devoted to manipulating and measuring micro-sized objects. Here a flexible microphotoluminescence (μ PL) custom-made setup has been built on purpose: every setup component has been optimized for 2D materials; an automatized system able to perform measurements in different positions of the sample and execute mapping have been made; the dependence of the μ PL intensity, peak center and other properties such as the Full Width Half Maximum (FWHM) on the position has been then extracted. The attention has been focused on WS_2 and phosphorene. Optical response has been compared between Chemical Vapor Deposition (CVD) grown WS_2 transferred on graphene and sapphire, especially focusing on the changes in the trion peak. Signatures have been found that can be attributed to photoluminescence from thick (more than five layers) phosphorene flakes.

1. Introduction

The discovery of graphene has paved the way for the utilization of the so called bidimensional (2D) materials: graphene exhibits exceptional transport, thermal, mechanical properties, but the lack of a gap restricts its field of application [1]; among others, transition metal dichalcogenides and phosphorene are instead largely used both for electronic and optical applications [1][2][3][4]. They can be obtained by exfoliation but also by Chemical Vapor Deposition (CVD), eventually accompanied by transfer on a particular substrate [5].

Transition metal dichalcogenides have a gap in the visible range: WS_2 , in particular, has a gap of 2.1 eV (for single layer[1]) which becomes indirect and shrinks with increasing thickness [1][6]. Phosphorene represents instead the ideal step in between graphene and metal dichalcogenides, exhibiting a gap (1 eV for free standing single layer[3]) going towards the near infrared [7]. Phosphorene gap is always direct [7] and increases with decreasing thickness. It is characterized by a strongly anisotropic structure, which justifies the interest from both a teoretical and an applicative point of view [4].

A flexible custom-made setup has been built on purpose with the aim to perform microphotoluminescence (μ PL) measurements on materials exhibiting optical properties lying in a very large spectrum region: every setup component has been optimized, and, in particular, the appropriate monochromator and detector were chosen for each material studied.



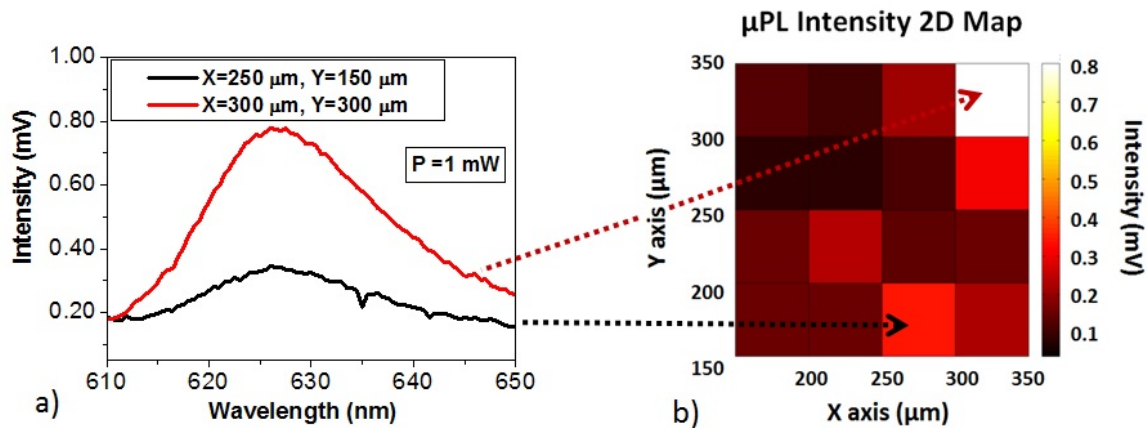


Figure 1. (a) Spectra of WS_2 μ PL acquired in two different positions of the sample and (b) the corresponding intensity map at 1 mW. The arrows highlight the correspondence between the measurements and the points on the map.

Microtranslators allowed to focus and to move on the sample with precision (i.e. few microns) even in presence of small flakes. Moreover, they gave the chance to build up a specific system capable of performing automatized μ PL measurements in different positions of the sample (e.g. see figure 1 (a)) and executing mapping. Maps have been obtained by fitting with one or more Lorentzian curves the μ PL peaks relative to different positions and then extracting the intensity (e.g. see figure 1 (b)), the peak center and other properties such as the Full Width Half Maximum (FWHM). Microphotoluminescence measurements and maps have been performed on different bidimensional materials, such as CVD grown WS_2 on sapphire and graphene and exfoliated phosphorene on SiO_2 . The optical properties have been studied in several different conditions, focusing on the peculiar features of the considered materials.

2. Materials and methods

WS_2 , phosphorene and $BaY_2F_8 : 10\%Er^{3+}$ doped samples have been gently provided respectively by Dr. C. Coletti, Dr. M.S. Vitiello, Prof. Tonelli and their research groups. More details on the experimental materials and methods can be found in [4][5][8].

The main elements of the flexible custom made μ PL setup are the following: green solid state laser (DJ532-40 Thorlabs) equipped with a cooled laser mount (TCDLM9 Thorlabs); 100x microscope (M-Plan Apo NIR 100x); lock-in (SR830); three microtranslation stages (two M-111 and a M-126, Mercury) assembled in a cascade system and controlled by three motor controllers (C863 and C862, Mercury); camera (Basler acA640-100gm); clean-up filter (Techspec OD-6 laser line), CWL 532 nm and Raman longpass edge filter (Techspec). The detection system has been changed from time to time and it will be clearly identified.

Since the samples were sensitive to environmental conditions (especially phosphorene [3]), a cleaning procedure (i.e. with toluene and nitrogen) has been developed, along with a system to perform and maintain vacuum (around 100 mbar) during measurements.

Before performing photoluminescence measurements on bidimensional materials, the setup has been tested on a well-known bulk material ($BaY_2F_8 : 10\%Er^{3+}$ doped). After that, microphotoluminescence (μ PL) maps have been performed on different CVD grown WS_2 on sapphire samples in order to test the setup. CVD grown samples have been preferred for the large measurable area available. Sapphire has been preferred as a substrate compared to graphene because of μ PL intensity quenching [9] (as will be discussed more widely in the

following section). In figure 1, μ PL map results have been shown: in figure 1 (a) two μ PL measurements collected in two different sample positions are reported while in figure 1 (b) the corresponding μ PL intensity map is shown. The monochromator was the HR250 Jobin Yvon; the photomultiplier Hamamatsu R943-02; cobalt attenuation filters were in place.

3. Discussion

3.1. Optical properties of WS_2 on graphene and sapphire

The interest in graphene is not only limited to the material in itself, but also as a substrate for other bidimensional materials, composing heterostructures with peculiar properties [2][16]. Tan et al. [9] have instead investigated the effect of the high carrier conductivity of graphene used as substrate for WS_2 : due to the migration of electrons in the underlying graphene, a quench in photoluminescence intensity has been experienced, accompanied by a decrease in the ratio of exciton/trion emission. The negative trion is a quasiparticle resulting from the combination of two electrons and a hole [10][11]. It came out to be an almost ubiquitous feature in bidimensional materials and, in particular, in transition metal dichalcogenides [2].

In our work, the optical properties of CVD grown single layer WS_2 on sapphire and on graphene have been compared, especially focusing on the trion peak. Measurements have been performed on the selected samples using QEpro or a HR250 and a Hamamatsu R943-02. In figure 2, μ PL curves measured have been shown. Both the samples have been measured immediately after fabrication and after 9 months. Best fits with two Lorentzian curves have been performed: the feature at lower wavelengths has been attributed to the neutral exciton (X), while the one at higher wavelengths to the negative trion (X^-) [9][12][13][14]. WS_2 on sapphire exhibits an exciton peak located at 620 nm, while on graphene it is located at 612 nm. Those values are generally in agreement with the literature, taking into account that variation between 620 and 640 nm can be found even in the same sample [6] and that a similar shift has been already measured on graphene [9]. Shifts in the position and in the Full Width Half Maximum (FWHM) can be attributed to several different factors, such as strain, doping, superficial defects [15][16]. The ratio of exciton/trion emission is higher for the sample on graphene, as expected [9]. The energy difference between the neutral exciton and the negative trion is in both cases around 30 meV (in agreement with literature [2][17]), irrespective of the different substrate.

The two samples have been measured several months after fabrication, and the spectra have been fitted with two Lorentzian curves. The trion feature is ubiquitously present in the sample on sapphire, even after 12 months from fabrication; on the other hand, in the sample on graphene the contribution of the trion after 9 months results negligible. Several factors can aid or hinder trion formation, such as thickness [18] or native doping [14]; nevertheless, it is probable that native doping during fabrication was comparable for the two samples. It is therefore reasonable taking into account the effects of the high conductivity of graphene in combination with WS_2 , and concluding that electron migration in the underlying substrate could be the preferential mechanism for trion annihilation in WS_2 on graphene.

3.2. Microphotoluminescence measurements on a thick phosphorene sample

Photoluminescence measurements on phosphorene are available in the literature for flakes thickness comprises between 1 and 5 layers [3][7][19][20]. Exceeding this limit means that gap goes into the infrared range and that intensity drops. For 6 or more layers phosphorene flakes, IR absorption was then used for investigating optical and thus electronic properties, even under the application of stress [7].

Here several thick (i.e. thicker than 5 layers) flakes have been measured. A HR250 and a nitrogen cooled InSb detector have been used. Since the μ PL intensity was expected to be low [19] measurements at high laser power have been performed, applying two different power intensities. Since measurements were performed under vacuum, damaging due to oxidation can

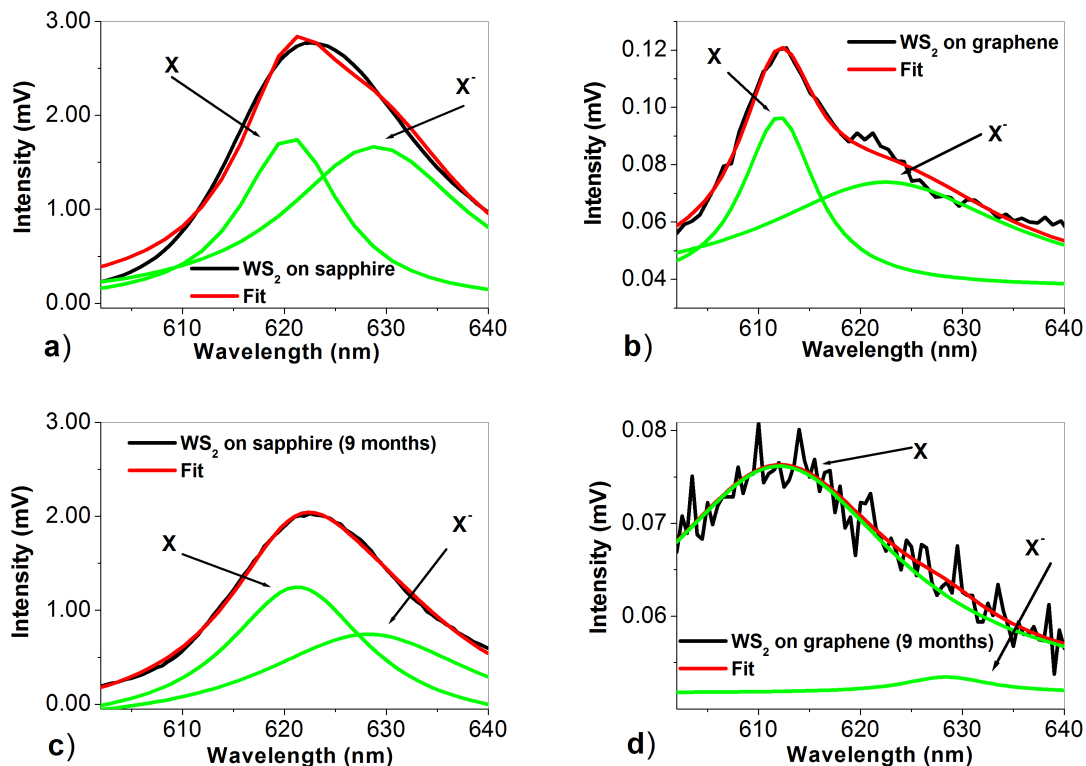


Figure 2. Microphotoluminescence curves measured on: WS_2 (a) on sapphire and (b) on graphene immediately after fabrication and (c) on sapphire and (d) on graphene after 9 months. Best fit with two Lorentzian curves evidence the neutral exciton (X) and the negative trion (X^-) peak.

be excluded [20].

In figure 3 hints are illustrated with the presence of a structure which tends to maintain its characteristics irrespective of the random nature of noise. In figure 3(a), the original spectra at different laser power and, in the inset, the flake picture. A 10 point smoothing was performed with three different smoothing techniques (FFT filter, adjacent averaging, Savitzky-Golay) and then fitted with two Lorentzian curves, with good agreement between them. In figure 3(b), the smoothed curves (with FFT filter) and the related Lorentzian fits are shown. It is possible to notice that the peak maintains its position irrespective of the increasing power, while the intensity increases, as expected [21]. Two features can be evidenced, respectively labeled as A (lower wavelength, lower intensity) and B (higher wavelength, higher intensity).

In bidimensional materials features at higher and lower energies than the gap have been widely reported [21] [22] and generally attributed to not intentional doping [7], to disorder or structural defects [2], to transitions between the lowest unoccupied molecular orbital (LUMO) and occupied molecular orbitals below the highest occupied molecular orbital (e.g. H-1 and H-2) [22]. The structure undergoes a slight shift at increasing power, which is in agreement with literature data on single layered and probably due to local laser heating [21]. Analogously, the not linear increasing of the μ PL intensity with power is also expected when high power is applied [21], as in our case.

μ PL results have been compared with the data available in the literature [19] (figure 3(c)), evidencing that the wavelength value of 1780 nm can be attributed to a 7 layers flake. In order

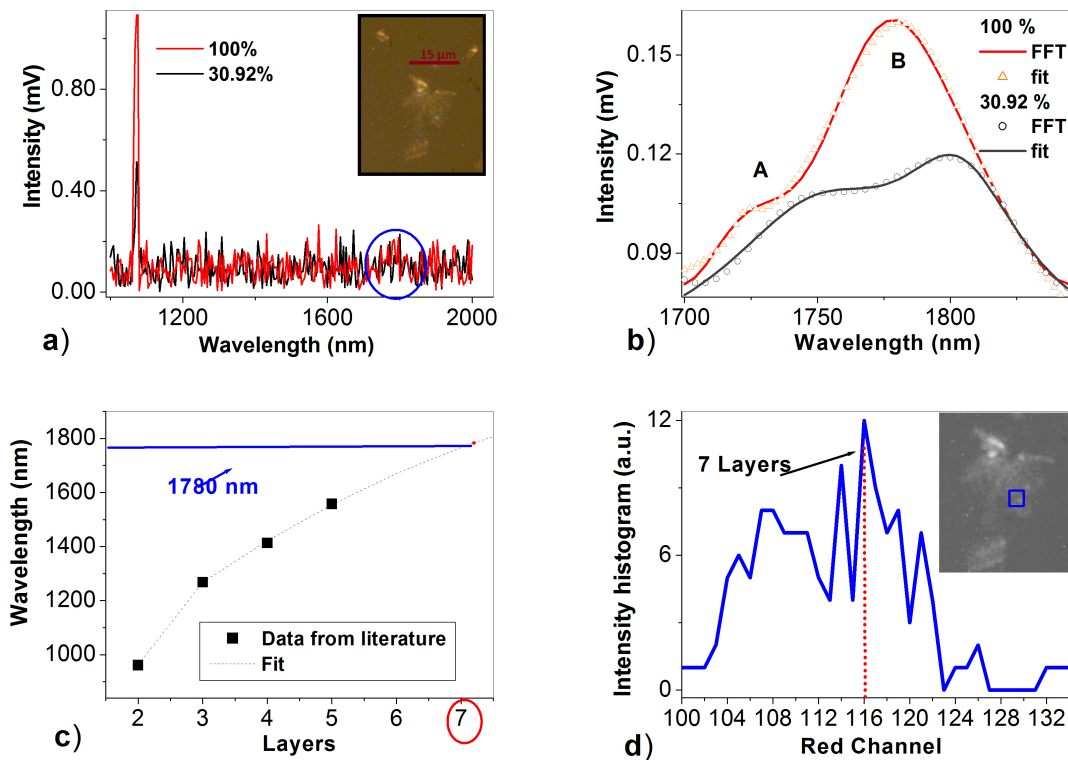


Figure 3. (a) μ PL spectra performed under vacuum at 30.92% and 100% of laser power of the flake showed in the inset. The picture of the flake was taken in-situ in the measurement setup, under vacuum. (b) 20 pt smoothing with FFT filter and fits. (c) Comparison with the literature data [19]. (d) Histogram of red channel intensity of the measured flake region.

to get more information regarding the thickness of the measured flake and verify the previous attribution, the optical image of the flake taken in situ has been considered. In the literature, optical contrast of flakes picture is a parameter routinely used for thickness determination [23][24]. Castellanos Gomez et al. [20] reported a similar procedure in which histograms of several different regions of the flake have been performed. Here, histograms of different regions of the flake have been extracted from the red channel picture. Histograms have been taken of the sole substrate, of a region almost completely single layer and of other regions in which multiple layers are present. From them, a correspondence between the intensity peak red channel value and the thickness has been obtained. As expected, the red value of increasing thicknesses is multiple at a constant value and no correspondence has been found between the substrate value and the flake ones. The main peak is located at red channel 116, the value which corresponds to 7 layers (figure 3(d)), in agreement with the comparison with the μ PL data found in the literature.

4. Conclusion

μ PL measurements have been performed on WS₂ and on phosphorene. In the first case, the spectra of WS₂ on sapphire and on graphene immediately after fabrication and after several months have been fitted with two Lorentzian curves and compared. The results suggest that electron migration plays a crucial role in the annihilation of the trion for WS₂ on graphene. In the second case, μ PL measurements have been performed on a thick phosphorene flake: a

structure whose characteristics are in agreement with the literature and which is compatible with a 7 layers phosphorene flake has been found. The position of the peak remains constant at increasing power while the intensity increases. A slight shift and the not linear intensity increase are in agreement with the literature. Comparison with μ PL data from the literature [19] suggests that the flake thickness could correspond to 7 layers, in agreement with the attribution of the thickness from histograms extracted from the optical image.

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