Spatially resolved optical absorption spectroscopy of single- and few-layer MoS$_2$ by hyperspectral imaging

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Abstract

The possibility of spatially resolving the optical properties of atomically thin materials is especially appealing as they can be modulated at the micro- and nanoscale by reducing their thickness, changing the doping level or applying a mechanical deformation. Therefore, optical spectroscopy techniques with high spatial resolution are necessary to get a deeper insight into the properties of two-dimensional (2D) materials. Here we study the optical absorption of single- and few-layer molybdenum disulfide (MoS$_2$) in the spectral range from 1.24 eV to 3.22 eV (385 nm to 1000 nm) by developing a hyperspectral imaging technique that allows one to probe the optical properties with diffraction limited spatial resolution. We find hyperspectral imaging very suited to study indirect bandgap semiconductors, unlike photoluminescence which only provides high luminescence yield for direct gap semiconductors. Moreover, this work opens the door to study the spatial variation of the optical properties of other 2D systems, including non-semiconducting materials where scanning photoluminescence cannot be employed.

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(Some figures may appear in colour only in the online journal)

1. Introduction

Atomically thin semiconductors hold the promise of complementing graphene in those applications where graphene’s lack of a band gap hampers its use. Single-layer molybdenum disulfide (MoS$_2$), the most studied 2D semiconductor to date [1–4], has already being applied in nanoelectronic devices like field-effect transistors [5], non-volatile memories [6–8] or logic circuits [9, 10]. The direct gap of single-layer MoS$_2$, in the visible range of the electromagnetic spectrum [11, 12], has also triggered the interest on its optical properties.

In the last few years, scanning confocal microscopy based optical spectroscopy techniques (especially microphotoluminescence) has made it possible to observe interesting optical phenomena such as quantum confinement induced direct-to-indirect band gap transition [11–13], photoluminescence emission from charged excitons [14–16] and valley-polarized photoluminescence yield [16–20]. Photoluminescence spectroscopy, however, is a very inefficient technique to study the optical properties of indirect band gap semiconductors (like few-layer MoS$_2$) and thus transmittance or absorption spectroscopy based techniques would be preferred instead. Nonetheless, spatially resolved absorption spectroscopy techniques are still very scarce and are mainly based on non-trivial modifications of expensive scanning confocal microscopy setups [21].
In this work we probe the local optical absorption of single- and few-layer MoS2 by hyperspectral imaging. This technique allows one to study the optical properties of MoS2 with diffraction limited spatial resolution in a very important range of the electromagnetic spectrum ranging from near-ultraviolet (NUV) to near-infrared (NIR) with interest for optoelectronics, night-vision imaging and photovoltaics. We find that this technique is especially convenient to study the optical properties of multilayer MoS2 and other indirect bandgap 2D materials that typically yield weak luminescence signals and thus are challenging to study with photoluminescence.

2. Experimental section

Atomically thin MoS2 samples have been prepared by mechanical exfoliation of bulk MoS2 (SPI Supplies, 429ML-AB) with Nitto tape (Nitto Denko Co., SPV224 clear). Poly(dimethylsiloxane) (PDMS) has been chosen as the substrate because of its transparency and its low interaction with MoS2. In fact, it has been recently shown that the optical properties of MoS2 on PDMS resembles those of free-standing MoS2 because of the reduced charge transfer between the PDMS and MoS2, much smaller than that of MoS2 on SiO2 [22].

In order to study the local optical absorption of the fabricated MoS2 flakes, we have developed a hyperspectral imaging setup by modifying an optical microscope (Nikon Eclipse LV-100), conventionally used in many laboratories to identify 2D materials. A fiber bundle is attached through the sample stage so transparent samples can be directly placed on top of the output of the bundle to be studied in transmission mode using the light emitted from the fibers (see the supporting information for more details). The bundle is connected to a tunable monochromatic light source (a combination of a tungsten lamp and a monochromator) which allows one to select the excitation wavelength with a bandwidth down to 1–2 nm. A monochrome CMOS camera (Edmund Optics, EO-5012 Monochrome USB 3.0 Camera) is attached to the trinocular of the microscope for detection. Note that this camera model does not incorporate the IR blocking filter (present in most CMOS cameras) making it possible to detect light with wavelength above 700 nm. A spectrum of the fiber bundle output light, measured with the monochrome camera through the microscope optics while the excitation wavelength is swept, is presented in the supporting information (figure S1) and it can be employed to determine the detectable photon energy range of the experimental setup: 1.2 eV to 3.3 eV (or 375 nm to 1030 nm). Figure 1(a) shows a cartoon of the experimental setup used for the hyperspectral imaging. Note that this setup can be implemented by relatively inexpensive (<15,000 $, including the cost of the white light source, the monochromator, the fiber bundle and the monochrome camera) modifications of a conventional optical microscope.

3. Results and discussion

The hyperspectral imaging is carried out by sweeping the excitation wavelength in steps and acquiring a transmission mode image for each wavelength. The collected data is then arranged in a 3D matrix, being the first two matrix indexes the X and Y spatial coordinates and the third index (λ) the wavelength (see the sketch in figure 1(b)). Spectral information of a certain sample region can be directly obtained by plotting all the elements along the wavelength dimension λ for given X and Y coordinates. This corresponds to a vertical cut along the wavelength axis in the matrix sketched in figure 1(b). Figure 1(c) shows a cartoon with two spectra extracted from two regions in the sample: bare substrate (red) and MoS2 (blue). Quantitative transmittance (T) information of the MoS2 region can be obtained by dividing both spectra: $T = \frac{I_{\text{flake}}}{I_{\text{sub}}}$ (see the inset in figure 1(c)), where $I_{\text{flake}}$ is the...
intensity acquired at a MoS$_2$ region and $I_{\text{subs}}$ the intensity measured onto the bare substrate. The absorbance $A$ can be obtained from the transmittance $T$ as: $A = -\log_{10}(T)$.

Figure 2 shows a sequence of transmission mode optical images of a mechanically exfoliated MoS$_2$ flake acquired at different excitation wavelengths, selected by the tunable monochromatic light source. Although the whole dataset comprises 123 images with illumination wavelength spanning from 375 nm to 1000 nm in 5 nm steps, this figure features six selected wavelengths. The first panel displays labels indicating the number of MoS$_2$ layers of the different regions of the flake. The dotted white line highlights the border of the MoS$_2$ flake to facilitate the comparison between images acquired at different wavelengths.

Figure 2. Wavelength dependent transmission mode images of MoS$_2$. Transmission mode optical microscopy images of a mechanically exfoliated MoS$_2$ flake acquired at different excitation wavelengths, selected by the tunable monochromatic light source. Although the whole dataset comprises 123 images with illumination wavelength spanning from 375 nm to 1000 nm in 5 nm steps, this figure features six selected wavelengths. The first panel displays labels indicating the number of MoS$_2$ layers of the different regions of the flake. The dotted white line highlights the border of the MoS$_2$ flake to facilitate the comparison between images acquired at different wavelengths.

Figure 3. Absorbance spectra of single- and few-layer MoS$_2$. Absorbance versus wavelength spectra, extracted from the sequence of images of a MoS$_2$ flake with regions of different thicknesses (ranging from single-layer to six-layers), acquired at different illumination wavelengths. The labels A, B and C indicate the features attributed to the generation of the A, B and C excitons. The inset shows a detail of the thickness dependent wavelength of the excitonic peaks.

In order to obtain quantitative spectral information, the sequence of 123 images is arranged as previously discussed for figure 1(b). Then, intensity versus wavelength spectra are extracted at certain positions on the sample (similarly to the cartoon example in figure 1(c)). All the spectra are normalized to an intensity versus wavelength spectrum, obtained from a bare substrate region close to the MoS$_2$ region of interest, to determine the optical transmittance $T(\lambda) = I_{\text{flake}}(\lambda)/I_{\text{subs}}(\lambda)$. The optical absorbance of MoS$_2$ flakes 1L to 6L thick, calculated from the transmittance values, as a function of the excitation wavelength are displayed in figure 3. The absorbance spectra have two prominent narrow peaks occurring at wavelengths $\sim$605 nm and $\sim$660 nm that correspond to the absorption due to the direct transitions at the K point of the Brillouin zone, associated with the generation of the B and A excitons respectively [11, 12]. While the position of the A exciton peak wavelength monotonically red-shifts with the number of layers, the B exciton peak wavelength remains almost unaltered (see the inset in figure 3). This observation is
thickness dependence of atomically thin MoS2 will be depends on the number of layers. A detailed study of the false color map displaying the position of the C and A exciton peaks, respectively, at the different regions of the MoS2 edge, separating two regions with a different number of lay-
erers, can be employed to estimate the spatial resolution. Below

edge, separating two regions with different number of layers, indicated with a white rectangle in (a) and (b). From the spatial variation of the exciton peak position in (c) and (d) one can estimate the spatial resolution: 300 nm for the C-exciton and 420 nm for the A-exciton (see the text for more details).

The spectra also show a broad peak around 440 nm. This feature is typically not observed in photoluminescence experiments which mostly use an excitation wavelength of ~300 nm. Recent reflectance and photocurrent spectroscopy experiments, however, present this feature (referred to as a C-exciton peak) whose origin is still a subject of debate [21, 23]. Interestingly, the position of this feature strongly depends on the number of layers. A detailed study of the thickness dependence of atomically thin MoS2 will be reported elsewhere.

The fact that hyperspectral imaging provides the optical transmittance/absorbance spectrum at every position of the flake can be exploited to generate maps where the spatial variation of a certain spectroscopic feature is probed. Figure 4 shows two maps displaying the spatial variation of the C and A exciton peak wavelength in the MoS2 sample shown in figure 2. By comparing figures 4(a) and (b) with figure 2 one can find a correspondence between the C and A exciton wavelength and the number of MoS2 layers, as discussed from the spectra acquired for the different number of layers (see figure 3).

A linecut of the exciton peak wavelength across a step-edge, separating two regions with a different number of layers, can be employed to estimate the spatial resolution. Below figures 4(a) and (b) two line profiles measured along the step-edges highlighted with a white rectangle are shown. The experimental line profiles can be reproduced by a step function with a Gaussian broadening of 300 nm (for the C-exciton) and 420 nm (for the A-exciton). These values are in good agreement with the maximum lateral resolution ($r$, smallest resolvable feature) of the optical microscope which for a diffraction limited microscope is expected to be between $r = 0.4 \times \lambda/NA$ and $r = 0.6 \times \lambda/NA$, where $\lambda$ the illumination wavelength ($\lambda \sim 440$ nm for the C-exciton and $\lambda \sim 660$ nm for the A-exciton) and NA the microscopic objective numerical aperture (NA = 0.8 in our experimental setup).

As discussed in figure 1(b), the collected hyperspectral data forms a 3D datacube ($\lambda = f(x, y, \lambda)$), that contains a great deal of information on the spatial distribution of the optical properties of the studied sample. However, 3D datasets cannot be easily visualized, and then one can present slices of data (figure 2), linecuts (figure 3) or compressed data (figure 4), losing significant fraction of the acquired information. Overcoming this problem is a subject of recent study in the field of hyperspectral imaging and some of the developed techniques (i.e. standard chemometric tools) could be applied to the acquired datasets to probe the spatial optical properties without losing information because of the representation [24–26].

4. Conclusion

In summary, we have locally probed the optical absorption of single- and multilayer MoS2 in an important range of the electromagnetic spectrum, spanning from 1.2 eV (NIR) to 3.3 eV (NUV). By developing a hyperspectral imaging technique, we are able to study the optical properties of these 2D semiconductors with diffraction limited spatial resolution. We demonstrate this high spatial resolution by mapping the excitonic features, present in the absorbance spectra, at different regions of the MoS2 sample. The hyperspectral imaging technique presented here can be applied to study a broad family of 2D materials and its high spatial resolution opens the door to study the effect on the optical properties of localized strain [27, 28], inhomogeneous chemical composition [29–31] or doping level [32] in 2D systems.

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References

[1] Wang Q H, Kalantar-Zadeh K, Kis A, Coleman J N and Strano M S 2012 Electronics and optoelectronics of two-dimensional transition metal dichalcogenides Nat. Nanotechnol. 7 699–712
[2] Fiori G, Bonaccorso F, Iannaccone G, Palacios T, Neumaier D, Seabaugh A, Banerjee S K and Colombo L 2014 Electronics based on two-dimensional materials Nat. Nanotechnol. 9 768–79

[3] Buscema M, Island J O, Groenendijk D J, Blanter S I, Steele G A, van der Zant H S J and Castellanos-Gomez A 2015 Photocurrent generation with two-dimensional van der Waals semiconductors Chem. Soc. Rev. 44 3691–718

[4] Lv R, Robinson J A, Schaak R E, Sun D, Sun Y, Mallouk T E and Terrones M 2015 Transition metal dichalcogenides and beyond: synthesis, properties, and applications of single- and few-layer nanosheets Acc. Chem. Res. 48 56–64

[5] Radisavljevic B, Radenovic A, Brivio J, Giacometti V and Kis A 2011 Single-layer MoS2 transistors Nat. Nanotechnol. 6 147–50

[6] Choi M S, Lee G-H, Yu Y-J, Lee D-Y, Lee S H, Kim P, Hone J and Yoo W J 2012 Controlled charge trapping by molybdenum disulphide and graphene in ultrathin heterostructured memory devices Nat. Commun. 4 1624

[7] Lee H S, Min S-W, Park M K, Lee Y T, Jeon P J, Kim J H, Ryu S and Im S 2012 MoS2 nanosheets for top-gate nonvolatile memory transistor channel Small 8 3111–5

[8] Bertolazzi S, Krasnozhon D and Kis A 2013 Nonvolatile memory cells based on MoS2/graphene heterostructures ACS Nano 7 3246–52

[9] Radisavljevic B, Whitwick M B and Kis A 2011 Integrated circuits and logic operations based on single-layer MoS2 ACS Nano 5 9934–8

[10] Wang H, Yu L, Lee Y-H, Shi Y, Hsu A, Chin M L, Li L-J, Dubey M, Kong J and Palacios T 2012 Integrated circuits based on bilayer MoS2 transistors Nano Lett. 12 4674–80

[11] Mak K F, Lee C, Hone J, Shan J and Heinz T F 2010 Atomically thin MoS2: a new direct-gap semiconductor Phys. Rev. Lett. 105 136805

[12] Splendiani A, Sun L, Zhang Y, Li T, Kim J, Chim C-Y, Galli G and Wang F 2010 Emerging photoluminescence in monolayer MoS2 Nano Lett. 10 1271–5

[13] Eda G, Yamaguchi H, Voiry D, Fujita T, Chen M and Chhowalla M 2011 Photoluminescence from chemically exfoliated MoS2 Nano Lett. 11 5111–6

[14] Mak K F, He K, Lee C, Lee G H, Hone J, Heinz T F and Shan J 2013 Tightly bound trions in monolayer MoS2 Nat. Mater. 12 207–11

[15] Ross J S et al 2013 Electrical control of neutral and charged excitons in a monolayer semiconductor Nat. Commun. 4 1474

[16] Tongay S, Zhou J, Ataca C, Liu J, Kang J S, Matthews T S, You L, Li J, Grossman J C and Wu J 2013 Broad-range modulation of light emission in two-dimensional semiconductors by molecular physisorption gating Nano Lett. 13 2831–6

[17] Jones A M et al 2013 Optical generation of excitonic valley coherence in monolayer WS2 Nano. Nanotechnol. 8 634–8

[18] Zeng H, Dai J, Yao W, Xiao D and Cui X 2012 Valley polarization in MoS2 monolayers by optical pumping Nat. Nanotechnol. 7 490–5

[19] Cao T et al 2012 Valley-selective circular dichroism of monolayer molybdenum disulphide Nat. Commun. 3 887

[20] Mak K F, He K, Shan J and Heinz T F 2012 Control of valley polarization in monolayer MoS2 by optical helicity Nat. Nanotechnol. 7 494–8

[21] Dhakal K P, Duong D L, Lee J, Nam H, Kim M, Kan M, Lee Y H and Kim J 2014 Confocal absorption spectral imaging of MoS2: optical transitions depending on the atomic thickness of intrinsic and chemically doped MoS2 Nano Lett. 13 13028–35

[22] Buscema M, Steele G A, van der Zant H S J and Castellanos-Gomez A 2014 The effect of the substrate on the Raman and photoluminescence emission of single-layer MoS2 Nano Res. 7 561–71

[23] Klots A R et al 2014 Probing excitonic states in suspended two-dimensional semiconductors by photocurrent spectroscopy Sci. Rep. 4 6608

[24] Duarte L T, Moussaoui S and Jutten C 2014 Source separation in chemical analysis: recent achievements and perspectives IEEE Signal Process. Mag. 31 135–46

[25] Bioucas-Dias J M and Plaza A 2011 An overview on hyperspectral unmixing: geometrical, statistical, and sparse regression based approaches 2011 IEEE Int. Geoscience and Remote Sensing Symp. pp 1135–8

[26] Bioucas-Dias J M, Plaza A, Dobigeon N, Parente M, Du Q, Gader P and Chanussot J 2012 Hyperspectral unmixing overview: geometrical, statistical, and sparse regression-based approaches IEEE J. Sel. Top. Appl. Earth Obs. Remote Sens. 5 354–79

[27] Feng J, Qian X, Huang C-W and Li J 2012 Strain-engineered artificial atom as a broad-spectrum solar energy funnel Nat. Photonics 6 866–72

[28] Castellanos-Gomez A, Roldán R, Cappelluti E, Buscema M, Guinea F, van der Zant H S J and Steele G A 2013 Local strain engineering in atomically thin MoS2 Nano Lett. 13 5361–6

[29] Huang C, Wu S, Sanchez A M, Peters J J P, Beanland R, Ross J S, Rivera P, Yao W, Cobden D H and Xu X 2014 Lateral heterojunctions within monolayer MoSe2-WSe2 semiconductors Nat. Mater. 13 1096–101

[30] Zhang X-Q, Lin C-H, Tseng Y-W, Huang K-H and Lee Y-H 2015 Synthesis of lateral heterostructures of semiconducting atomic layers Nano Lett. 15 410–5

[31] Gong Y et al 2014 Vertical and in-plane heterostructures from WS2/MoS2 monolayers Nat. Mater. 13 1135–42

[32] Ross J S et al 2014 Electrically tunable excitonic light-emitting diodes based on monolayer WS2/p-n junctions Nat. Nanotechnol. 9 268–72