Optical Identification of Single- and Few-Layer MoS_2 Sheets

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Two-dimensional (2D) layered nanomaterials have attracted increasing attention in recent years due to their unusual electronic and physical properties.[1–30] Among them, graphene, a single-layer 2D carbon material, has attracted enormous interest in both fundamental studies and potential applications.[1,2,4–6,30] Other 2D semiconducting dichalcogenides, such as MoS_2, have also attracted significant research interest and show great potential applications.[1,3,7–24] Many methods have been reported to prepare the 2D layered nanomaterials, which include micromechanical cleavage,[1,6,18,21,22,25–29,31] chemical vapor deposition,[32] solution-based exfoliation,[12,16,20,23,24] and our recently developed simple but highly effective electrochemical lithiation process.[3] To date, micromechanical cleavage is still the easiest and fastest way to obtain highly crystalline, atomically layered sheets of 2D nanomaterials.[1,2,18,21,22,31,33,34]

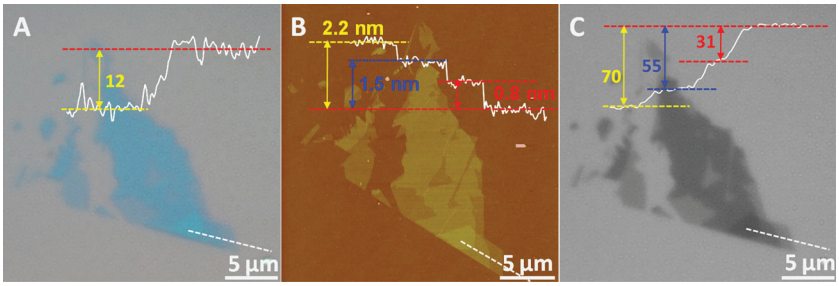

Figure 1. Optical and AFM images of an MoS_2 flake consisting of 1L, 2L, and 3L sheets. A) Color optical image. Inset: Contrast profile of the dashed line showing the intensity difference between the MoS_2 flake and 300 nm SiO_2 substrate. B) AFM image. Inset: Height profile of the dashed line. C) Grayscale image of the R channel extracted from (A). Inset: Contrast profile of the dashed line showing the intensity difference between the MoS_2 flake and 300 nm SiO_2 substrate.

The electronic properties of 2D layered nanomaterials are highly related to their thickness. Thus, the location and identification of the layer numbers of graphene and dichalcogenides is the first priority to enable the practical applications of these layered materials. Currently, many methods have been well established to identify the layer number of graphene, which include scanning probe microscopy (SPM),[1,4–6,30] scanning electron microscopy (SEM),[35] transmission electron microscopy (TEM),[36] Raman spectroscopy,[33,37–41] and optical microscopy.[34,35,42–50] Among them, Raman spectroscopy and optical microscopy can provide a rapid identification of single- and few-layer graphene sheets. However, it is still a challenge to identify the layer number of thin MoS_2 sheets rapidly and accurately using Raman spectroscopy, as the difference between double-layer and several-layer MoS_2 sheets is ambiguous and not obvious in Raman spectra.[10,22] Furthermore, until now there has been a paucity of reports on the identification of 2D layered dichalcogenide crystals by optical microscope,[18,51] especially the accurate identification of their layer number.

Herein, we present a simple, but rapid and accurate approach to identify the layer number of 2D layered MoS_2 sheets on a 300 nm SiO_2 substrate by using an optical imaging method combined with image analysis software (Image J). After the color optical image of MoS_2 sheets is split into the monochromic red (R), green (G), and blue (B) channels using the Image J software, the high-contrast grayscale image of MoS_2 sheets can be found in the R channel. The intensity difference between the MoS_2 sheets (from single layer to triple layer) and 300 nm SiO_2 in the R channel increases with the layer number of MoS_2, which can be used to identify the layer number of MoS_2 sheets. Atomic force microscopy (AFM) and Raman spectroscopy were also used to confirm the results obtained by the optical images.

In a typical experiment, we first used an optical microscope with a white-light source to locate the MoS_2 flake, obtained by the scotch tape-based mechanical exfoliation method,[22] and identify the layer number with the naked eye. AFM was then used to image the MoS_2 flake. **Figure 1**A shows the color optical image of a thin MoS_2 flake consisting of single- (1L), double- (2L), and triple-layer (3L) MoS_2 sheets (confirmed by AFM measurement in Figure 1B). As shown by the intensity profile (inset in Figure 1A), the value of the intensity difference between the 3L MoS_2 sheet

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DOI: 10.1002/smll.201101958

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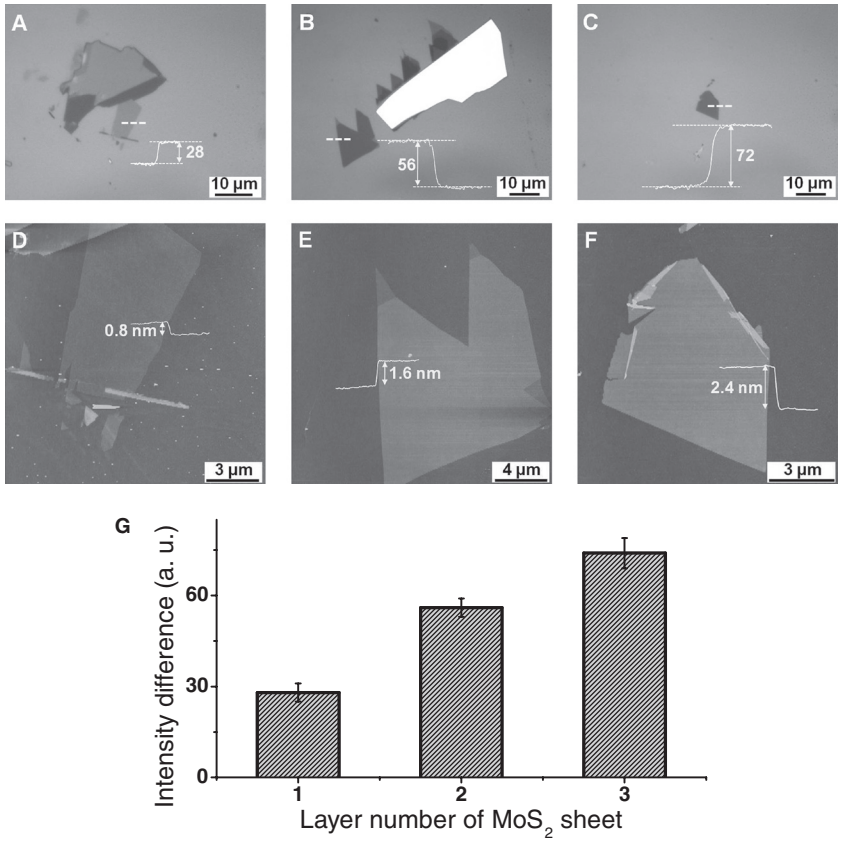

Figure 2. Grayscale images of the R channel of A) 1L, B) 2L, and C) 3L MoS_2 sheets and D–F) the corresponding AFM images. The inset in each image is the corresponding contrast profile or height profile. G) Statistical data of the intensity difference between MoS_2 sheets (1L, 2L, and 3L) and the 300 nm SiO_2 substrate.

(further confirmed by AFM measurement in Figure 1B) and the 300 nm SiO_2 substrate is 12 and the boundaries among the 1L, 2L, and 3L MoS_2 sheets are ambiguous. Therefore, it is difficult to identify the different atomic planes of the MoS_2 flake from the color optical microscopy image.

It has been reported that the layer numbers of single- and few-layer graphene sheets can be determined by analyzing their intensity difference in the grayscale image converted from the color optical image,[50] but this method does not work on the 1L to 3L MoS_2 sheets (Figure S1A,B in the Supporting Information). However, we found that after the color optical image of MoS_2 flake (Figure 1A) was split into the grayscale images of R, G, and B channels using the Image J software, the grayscale image of the R channel showed a high-contrast image of the MoS_2 flake (Figure 1C), while that of G or B channels showed low-contrast images (Figure S1C,D in the Supporting Information). As shown in Figure 1C, the 1L, 2L, and 3L MoS_2 sheets (confirmed by AFM in Figure 1B) can be clearly distinguished and the intensity profile (inset in Figure 1C) shows three clearly observed steps, which correspond to the different layers of MoS_2 sheets.

AFM was further used to image the same MoS_2 flake shown in Figure 1A and C. The height profile clearly showed that the thickness of the three steps is 0.8, 1.5, and 2.2 nm (Figure 1B), which is consistent with the height of 1L, 2L, and 3L MoS_2 sheets, respectively.[22] These data confirm that the three steps in the intensity profile shown in Figure 1C correspond to the 1L, 2L, and 3L MoS_2 sheets. The values of the intensity difference between the MoS_2 sheet and 300 nm SiO_2 substrate (inset in Figure 1C) are 31 for 1L MoS_2, 55 for 2L MoS_2, and 70 for 3L MoS_2.

To give quantitative and statistical characterization of the layer numbers of MoS_2 sheets, a large number of MoS_2 flakes (total 77 flakes) with layer numbers ranging from 1L to 3L, prepared by the mechanical cleavage technique,[22] were measured by optical microscopy and AFM. **Figure 2**A–C show the typical optical images of individual 1L (Figure 2A), 2L (Figure 2B), and 3L (Figure 2C) MoS_2 sheets. The value of the intensity difference between these MoS_2 sheets and the 300 nm SiO_2 substrate is 28 for 1L MoS_2, 56 for 2L MoS_2, and 72 for 3L MoS_2 (insets in Figure 2A, B, and C, respectively). Figure 2D–F shows the corresponding AFM images, which further confirmed the layer numbers of the corresponding MoS_2 sheets (Figure 2A–C), that is, 0.8 nm for 1L, 1.6 nm for 2L, and 2.4 nm for 3L MoS_2. The statistical data of the value of intensity difference between the MoS_2 sheet and substrate with respect to different

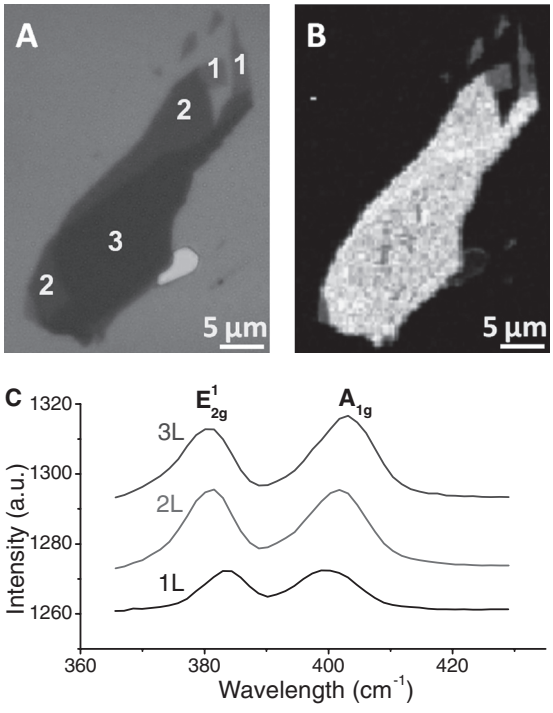

Figure 3. A) Grayscale image of the R channel and B) Raman mapping of an MoS_2 flake. Three regions with different contrast marked by 1, 2, and 3 correspond to 1L, 2L, and 3L MoS_2 sheets, respectively. C) Raman spectra of 1L, 2L, and 3L MoS_2 sheets.

layer numbers are plotted in Figure 2G, which shows that the values of intensity difference for 1L, 2L, and 3L MoS_2 sheets are 28 ± 3, 56 ± 3, and 74 ± 5, respectively. Therefore, our method provides a quantitative fingerprint to distinguish the layer number (1L to 3L) of MoS_2 sheets on the 300 nm SiO_2 substrate.

Moreover, Raman spectroscopy was used to confirm the successful identification of the layer number of MoS_2 by using the aforementioned method. **Figure 3**A shows the grayscale image of the R channel of an MoS_2 flake. It is clearly observed that the MoS_2 flake has three regions with different contrast marked by 1, 2, and 3, which corresponded to 1L, 2L, and 3L MoS_2 sheets, respectively, confirmed by our aforementioned method. The Raman spectra of the marked regions (Figure 3C) further confirmed the layer numbers of the MoS_2 flakes. The 1L MoS_2 sheet exhibits strong bands at 384 and 400 cm^{-1}, which are associated with the in-plane vibration (E^1_{2g}) and out-of-plane vibration (A_{1g}) modes, respectively. As the layer number increases from 1L to 3L (Figure 3C), a red shift of the E^1_{2g} band and a blue shift of the A_{1g} band were observed, which is consistent with previous reports.[10,22] However, in the Raman mapping (Figure 3B), although 1L and 2L of MoS_2 sheets can be easily identified, the contrast between 2L and 3L MoS_2 sheets is quite low.

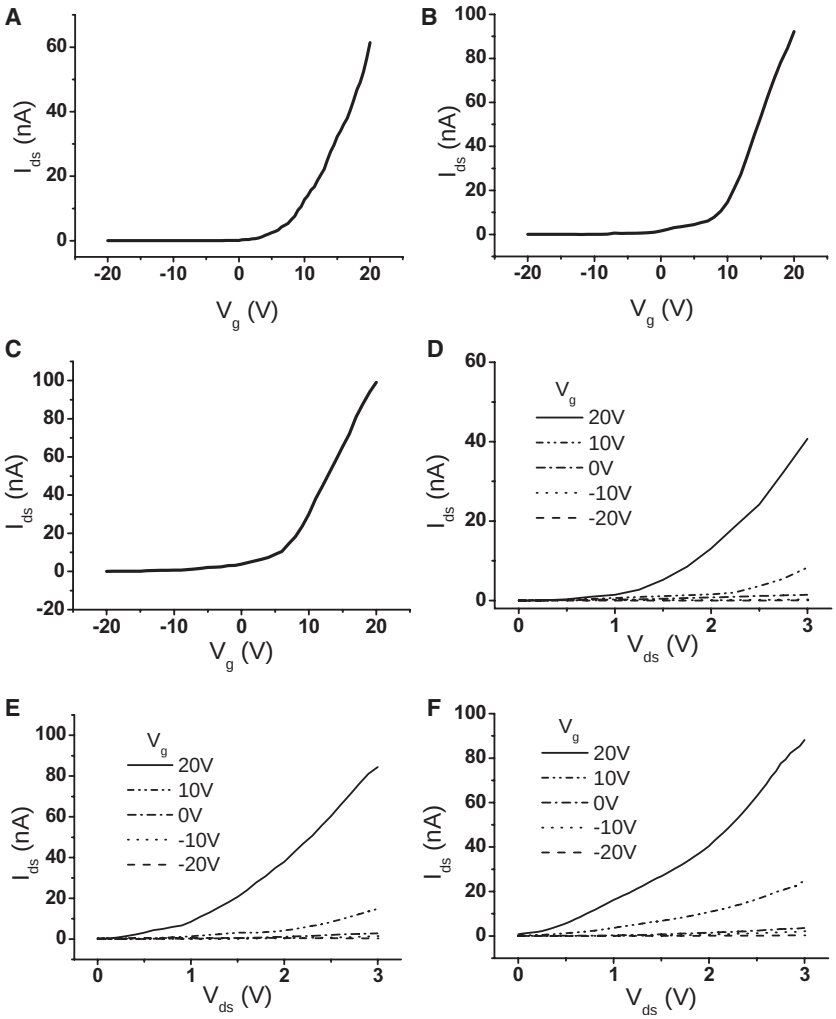

Figure 4. A–C) Plots of I_{ds} versus V_g of A) 1L, B) 2L, and C) 3L MoS_2-based FETs at V_{ds} = 3 V. D–F) I_{ds}–V_{ds} curves of D) 1L, E) 2L, and F) 3L MoS_2-based FETs at different V_g from −20 to +20 V.

To study the electrical properties of different layered MoS_2 sheets, field-effect transistors (FETs) were fabricated. The recorded I_{ds}–V_g characteristic curve (**Figure 4**A) is typical of a 1L MoS_2 FET with an n-type channel, which is in agreement with previous reports.[10,22] Similarly, the 2L and 3L MoS_2 FETs also showed the n-type doping characteristic (Figure 4B and C). The current On/Off ratio of the fabricated 1L, 2L, and 3L MoS_2 devices is above 10^3 (V_g ranging from –20 to +20 V, Figure 4A–C). Figure 4D–F shows the I_{ds}–V_{ds} curves of 1L to 3L MoS_2 FETs at V_g from –20 to +20 V.

In summary, a simple approach is developed to rapidly and accurately identify 1L to 3L MoS_2 sheets on a 300 nm SiO_2 substrate by using an optical microscopy imaging method combined with the Image J software. The grayscale image of the R channel, which is extracted from the color optical image, shows a high-contrast image of the MoS_2 sheet with thickness ranging from 1L to 3L. The value of the intensity difference between MoS_2 sheets (1L to 3L) and the 300 nm SiO_2 substrate in the grayscale image of the R channel is successfully used to identify the layer number of MoS_2 sheets quantitatively. AFM and Raman spectroscopy are also used to confirm the data obtained by the aforementioned method. Our technique provides an effective and quantitative fingerprint to quickly and accurately distinguish the 1L to 3L MoS_2 sheets on the 300 nm SiO_2 substrate, which is useful in device fabrication using different layered MoS_2 sheets.

Experimental Section

Mechanical Exfoliation of MoS_2: Single- and few-layer MoS_2 sheets were isolated from a bulk MoS_2 sample (429MM-AB, molybdenum disulfide, single crystals from Canada, SPI Supplies) and then deposited onto freshly cleaned Si substrates covered by a 300-nm-thick SiO_2 layer by using the scotch tape-based mechanical exfoliation method,[22] which is widely employed for the preparation of single-layer graphene sheets.

Optical Microscopy Imaging and Data Analysis Using Image J Software: First, an optical microscope (Eclipse LV100D with a 100×, 0.9 numerical aperture (NA) objective, Nikon) equipped with a color camera (Nikon DS-Fi1) was used to locate and identify the 1L to 3L MoS_2 sheets with the naked eye. The color optical images of 1L to 3L MoS_2 sheets were captured by using the NIS Elements software (NIS-Elements F Package Ver. 3.00, Nikon). To calibrate and obtain the color images of MoS_2 sheets with a similar contrast, the "autowhite" command was applied before the images were captured.

The color optical images of 1L to 3L MoS_2 sheets were opened by the Image J software (version 1.45o, National Institutes of Health, USA), and the grayscale image of the R channel was extracted by using the "Split Channels" command from "Image>Color>Split Channels" in the menu. In the grayscale image of the R channel, we dragged the left button of the mouse to draw a line across the atomically thin MoS_2 sheet and then pressed "Ctrl+K" to obtain the line profile of intensity difference. In the plot of the line profile, we clicked "List" to show the intensity values of the MoS_2 sheet and SiO_2 substrate.

AFM Images and Raman Spectroscopy: AFM (Dimension 3100 with Nanoscope IIIa controller, Veeco, CA, USA) was used to image the MoS_2 sheets in tapping mode in air and confirm the layer number by measuring the thickness of the MoS_2 sheets. Analysis of 1L to 3L MoS_2 sheets by Raman spectroscopy was carried out on a WITec CRM200 confocal Raman microscopy system with the excitation line of 488 nm and an air-cooled charge-coupled device (CCD) as the detector (WITec Instruments Corp., Germany). The Raman band of a Si wafer at 520 cm^{-1} was used as a reference to calibrate the spectrometer.

Fabrication and Characterization of MoS_2 FETs: The source and drain electrodes of MoS_2 FET devices were fabricated by the traditional photolithography. The channel length for all FET devices was kept at ≈3 μm. The 5 nm Ti/50 nm Au source and drain electrodes were deposited by using an electron-beam evaporator. After removal of the photoresist with acetone and subsequent thermal annealing at 200 °C for 2 h in the mixture of Ar:H_2 (v/v=9:1),[22a] the electrical properties of 1L to 3L MoS_2 FETs were tested by the Keithley 4200 semiconductor characterization system in air at room temperature.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was supported by AcRF Tier 2 (ARC 10/10, No. MOE2010-T2-1-060) from MOE, the Singapore National Research Foundation under CREATE programme: Nanomaterials for Energy and Water Management, and the New Initiative Fund FY 2010 (M58120031) from NTU in Singapore.

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Received: September 20, 2011
Published online: January 5, 2012