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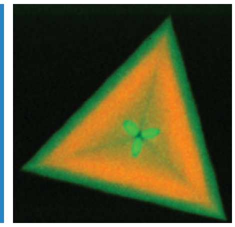
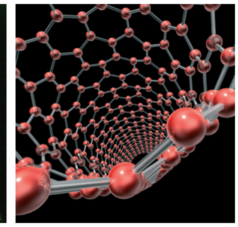
Raman Spectroscopy

Combined Raman and Photoluminescence Imaging of 2D WS_2





Application Note

Nanotechnology RA67

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Abstract

Raman and photoluminescence spectroscopy and imaging are used to examine the spatial variation of solid state structure and electronic character of two dimensional (2D) WS_2 crystals. Simultaneous acquisition of photoluminescence spectra with the Raman scattering provides complementary ways of rendering Raman and photoluminescence spectral images of thin film WS_2.

Keywords: Raman and photoluminescence spectroscopy, 2D materials, WS_2

Raman and Photoluminescence Imaging of 2D WS_2

Graphene is probably the most well-known of the emerging class of materials known as two-dimensional crystals. These materials are constituted by monolayer to few-layered structures. In recent years, **new inorganic two dimensional materials have emerged including MoS_2, $MoSe_2$, WS_2, WSe_2 among others.** These materials have attracted significant interest because of special electronic, optical and optoelectronic properties in the monolayer to few-layer forms that are different from those manifest by the bulk form (1, 2). One of the most significant differences of the two-dimensional crystals is the transformation from an indirect band gap semiconductor in the bulk to a direct band gap semiconductor in the monolayer to few-layer crystals. Thus, the fabrication of optoelectronic devices in addition to familiar integrated electronic circuitry is envisioned for these materials. These optoelectronic characteristics have prompted substantial research to discover the means of fabrication and the physical characteristics of two-dimensional crystals to produce integrated electronic and optoelectronic devices (3).

You may have observed the spatially varying colors in reflected white light images of 2D crystals, and so there have been developments to use optical microscopy to rapidly identify the number of molecular layers that make up the two-dimensional crystal (4). Previously, we reported on the use of resonance Raman and photoluminescence spectroscopy and imaging of few-layer MoS_2 to identify spatial variation in the number of layers and strain (5). **In this Application Note, we focus on Raman and photoluminescence (PL) imaging for the characterization of 2D WS_2 crystals.**

Experiment

The Raman and PL data were acquired with a **LabRAM HR Evolution using 532 nm excitation** in conjunction with a 300 gr/mm grating and a 50X Olympus objective and by moving the stage in 1.5 µm increments over an area of approximately 100 µm x 100 µm. The combined Raman and photoluminescence image is actually a rendering of signal strength for the Raman band at 349 cm^{-1} and the photoluminescence band centered at 630 nm as a function of position on the sample.

The triangular crystal consists primarily of a single layer of WS_2 with a three-pronged two-layer formation growing out from the center. The two-layer formation appears as the darker purple structure in the white light image and appears brighter green in the combined Raman and PL spectral image.

Results

Here, **we apply Raman and photoluminescence imaging to compare the spectral and structural differences** revealed through spectroscopy to the contrast observed when viewing the crystals with reflected white light microscopy. A collection of **hyperspectral data** from a 2D WS_2 crystal is shown in Fig. 1. A reflected white light image of the crystal appears in the lower right hand corner and a combined Raman and photoluminescence image corresponding to the reflected light image appears to its left. The plot on the upper left consists of all of the Raman and photoluminescence spectra acquired over the image area and the upper right hand plot is of the single spectrum associated with the cross hair location in the Raman and reflected light images.

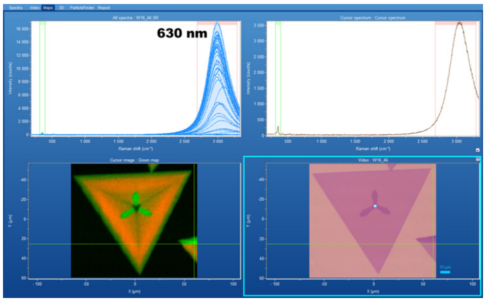

Figure 1: Combined Raman and photoluminescence image (lower left), reflected white light image (lower right), hyperspectral data set (upper left) and cursor spectrum (upper right) of 2D WS_2 crystal.

In Fig. 2, the combined spectral image is rendered through a color coded plot of Raman (green) and photoluminescence (red) signal strength over the corresponding color bracketed Raman shift positions shown in the upper traces. The perimeter of the crystal appears green because of the absence of photoluminescence at that location. The separate Raman and photoluminescence images in Fig. 2 show the spatially varying differences in solid state structure as revealed through vibrational and electronic spectroscopies.

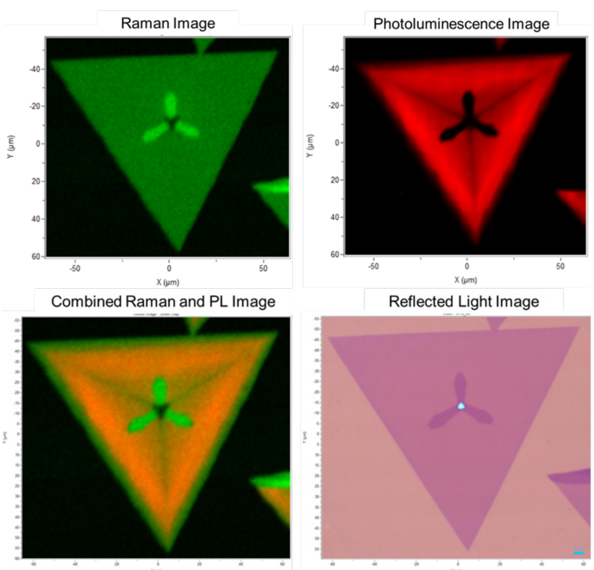

Figure 2: Raman (upper left) and photoluminescence (upper right) images of 2D WS_2. Combined Raman and photoluminescence image (lower left) and reflected white light image of 2D WS_2 (lower right).

Conclusion

Raman and photoluminescence spectroscopy reveal different aspects of the solid state structure of 2D materials. Raman and photoluminescence imaging performed simultaneously with one instrument reveals the spatial variation of the solid state structure and electronic properties of 2D crystals that is not revealed in reflected white light imaging. That ability should allow materials scientists to better design and fabricate electronic and optoelectronic devices based upon 2D crystals.

The two-layer formation appears brighter in the Raman image and the rest of the crystal appears fairly uniform. However, the photoluminescence image consists of a dark three-fold axis with diminished photoluminescence in the surrounding area. The two-layer formation yields very weak emission. These structural variations are revealed in the combined Raman and photoluminescence of other crystals as shown in Fig. 3.

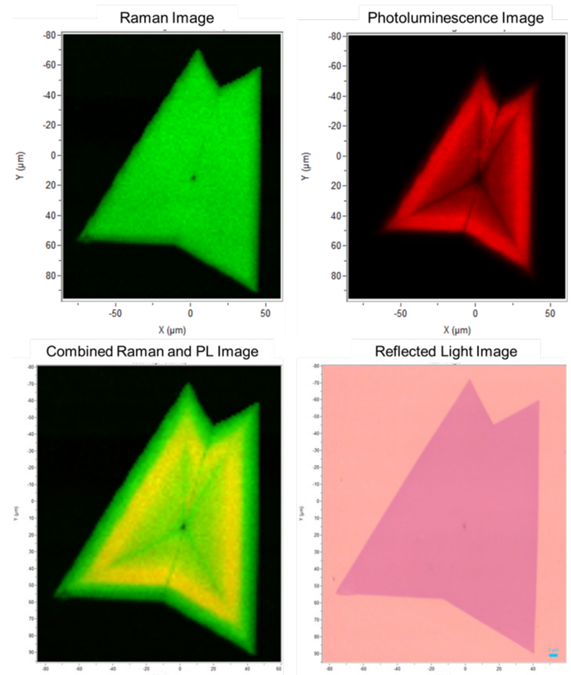

Figure 3: Raman (upper left) and photoluminescence (upper right) images of 2D WS_2. Combined Raman and photoluminescence image (lower left) and reflected white light image of 2D WS_2 (lower right).

References

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Acknowledgement

This work was performed in collaboration with Prof. Davood Shahrjerdi and Abdullah Sanad M. Alharbi of New York University.

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