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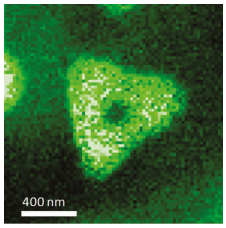
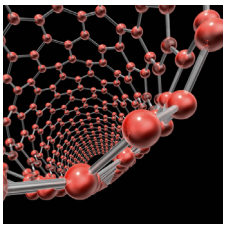
Raman Spectroscopy

Characterization of MoS_2 Flakes using Tip-Enhanced Optical Spectroscopies (TEOS)





Application Note

Materials RA63

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Keywords
MoS_2 - 2D materials - Tip-Enhanced Raman Spectroscopy - Tip-Enhanced Photoluminescence

Context and issues

Molybdenum disulfide (MoS_2) is a promising semiconducting Transition Metal Dichalcogenide (TMD) 2D nano-material for next generation photovoltaic solar cells, optoelectronic circuits and sensors due to its great excitonic recombination property, high carrier mobility and low leakage current. One of the advantages of two dimensional (2D) TMDs, when compared to graphene, comes from quantum confinement, enabling the indirect-to-direct bandgap transition as a function of number of individual layers. Nano-scale characterization is needed for the understanding necessary to engineer nanodevices integrating monolayer MoS_2.

Potential / Input from technique

Tip-enhanced optical spectroscopies (TEOS) based on the amplification of signal from the nano-region under the tip enables such nano-characterization. In the case of 2D TMD, Tip-Enhanced Photoluminescence (TEPL) is capable of revealing variation in emission within a submicron size flake. Complementary morphological, chemical, and electronic structure information may be acquired simultaneously and with nanometer spatial resolution through AFM imaging, Tip Enhanced Raman spectroscopy (TERS) and Kelvin probe measurements, respectively.

Starting point, what is known?

Monolayer MoS_2 has a bandgap of about 1.8 eV, which is observed through photoluminescence (PL) spectroscopic analysis. The PL spectrum may be decomposed as two peaks due to excitonic features: the A_0 mode derived from an exciton consisting of one electron and one hole bound by Coulomb interaction and the A^- mode derived from a trion, a charged three body exciton, consisting of an exciton combined with another electron. It has been reported that the PL intensity decreases with the increasing number of MoS_2 layers and that the PL intensity to Raman intensity ratio is related to the number of layers.

Description of sample and measurement

This application note presents tip enhanced data obtained on MoS_2 directly grown on a SiO_2/Si substrate using chemical vapor deposition. A NanoRaman™ system from HORIBA Scientific combining an Atomic Force Microscope (SmartSPM) with a Raman spectrometer (LabRam HR Evolution) is used in a reflection configuration (objective lens ×100, NA = 0.7) with a 60° angle with respect to sample surface. A *p*-polarized 594 nm laser light is focused onto the apex of the cantilever-based silver TERS tip.

The set of data (TEPL, and TERS) shown in *Figure 1* was obtained on a flake of MoS_2. The PL intensity to Raman intensity ratio from the spectrum (acquisition time/pixel: 0.5 s) indicates that the flake is monolayer MoS_2.

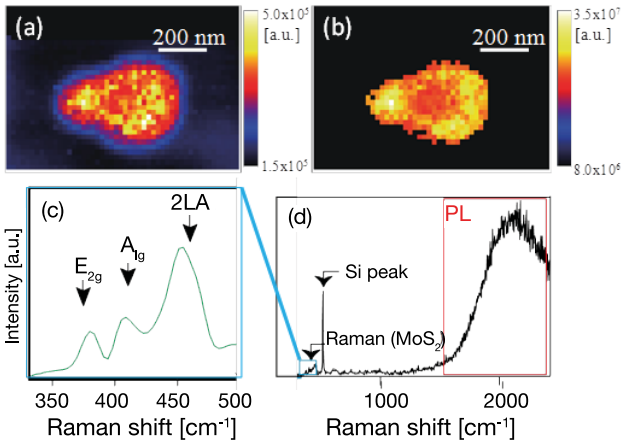

Figure 1: (a) TERS image constructed from integrating signal from 420 to 450 cm⁻¹, (b) TEPL image on a single layer MoS_2 flake taken simultaneously, (c) TERS spectrum featuring normal vibration modes: E_{2g}, A_{1g} and 2LA, and (d) full spectrum including TERS peaks and TEPL broad peak.

The TEPL shift image derived from fitting the PL peak through regression analysis is shown in *Figure 2* and reveals differences between: the *edge* of the flake *(blue shift)* and the *center* of the flake *(red shift)*. This truly localized phenomenon can be explained by the relative difference in excitons and trions in these different regions of the flake. Deconvolution of the PL peak into A_0 and A^- contributions may yield spatial variations of their relative intensity which can be interpreted as local electronic band structure change (local shift of the Fermi energy).

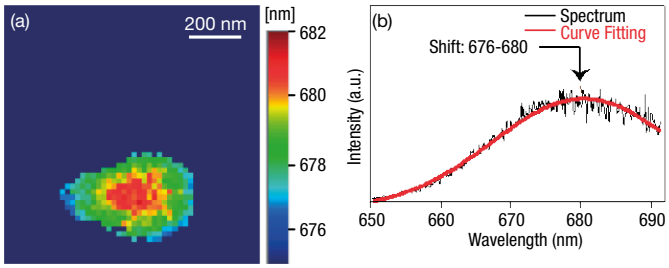

Figure 2: (a) TEPL-shift image and (b) Curve Fitting of PL signal.

On the same sample, additional information about surface potential has been acquired on an area containing both monolayer and bilayer MoS_2 flakes (*Figure 3*). PL intensity and TERS (through separation between A_{1g} and E_{2g} peaks) consistently distinguish monolayer and bilayer flakes. Also, the *Kelvin probe* force map shows *positive* values around 100 mV for *bilayer* flakes, and *negative* values around -300 mV for *monolayer* flakes. This indicates that the Fermi energy increases in bilayer MoS_2. A higher Fermi level is possibly attributed to a modification of the electronic band structure, leading to a PL process change from direct bandgap to indirect bandgap.

Conclusion and perspectives

Both TEPL and TERS images are well correlated with AFM morphological images obtained simultaneously, and all are consistent in revealing the nature (number of layers) of MoS_2 flakes. Upon deconvolution, the TEPL signal is even capable of revealing local inhomogeneities within a MoS_2 flake of 100 nm size. *Kelvin probe* measurement supports TEPL and TERS measurements and adds to the power of such tip-enhanced combinative tools.

TEOS characterization of 2D materials is likely to contribute to further deployment of these materials into commercial products through a better understanding of their electrical and chemical properties at the nanoscale.

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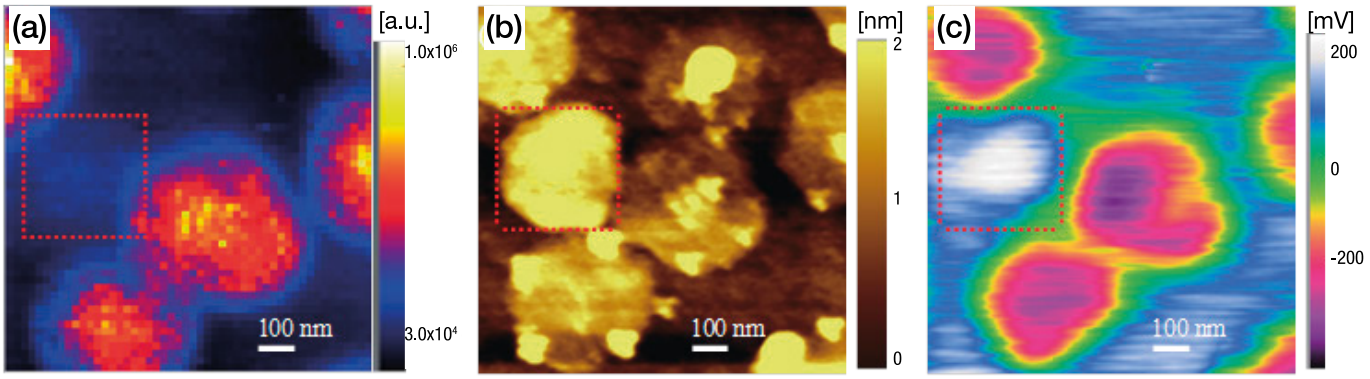

Figure 3: (a) TEPL map, (b) AFM image of monolayer and bilayer MoS_2 flakes and (c) Kelvin force image (same area as images (a) and (b)).

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