Raman Spectroscopy

Characterization of MoS$_2$ Flakes using Tip-Enhanced Optical Spectroscopies (TEOS)

Agnès Tempez, Yoshito Okono, Marc Chaigneau
HORIBA Scientific, Avenue de la Vauve, Passage Jobin Yvon, 91120 Palaiseau, France

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Context and issues

Molybdenum disulfide (MoS$_2$) is a promising semiconducting transition metal dichalcogenide 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, e.g. with respect to graphene, comes from quantum confinement, enabling the indirect-to-direct band-gap transition as a function of number of individual layers. Nano-scale characterization is needed for better understanding necessary for engineering 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 will allow for actual 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 band gap about 1.8 eV, which is observed through photoluminescence (PL) spectroscopic analysis. The PL spectrum is decomposed in two peaks due to excitonic features: the $A_1$ mode derived from an exciton consisting of one electron and one hole bound by Coulomb interaction and the $A$ mode derived from a trion, charged three body excitons, consisting of an exciton combined with another electron. It has been reported that the PL intensity decreases with 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 is obtained on a flake of MoS$_2$. The PL intensity to Raman intensity ratio from the spectrum (acquisition time/pixel: 0.5 s) indicate that the flake is monolayer MoS$_2$.

![Figure 1](image-url)

**Figure 1:** (a) TERS image constructed from integrating signal from 420 to 450 cm$^{-1}$, and (b) TEPL image on a single layer MoS$_2$ flake taken simultaneously. (c) TERS spectrum featuring normal vibration modes: $E_{2g}$, $A_1$, 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 evidences spatial differences: blue shift at the edge of the flake versus red shift in the center. This truly localized phenomenon can be explained from relative difference in excitons and trions appearing in 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](image2.png)

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

On the same sample, additional information about surface potential has been acquired on an area comprising individual monolayer and bilayer MoS$_2$ flakes (Figure 3). PL intensity, and TERS (through separation between $A_{1g}$ and $E_{2g}$ peaks) are consistent in distinguishing monolayer and bilayer flakes. Plus 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.

![Figure 3](image3.png)

**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)).

### Conclusion and perspectives

Both TEPL and TERS images are well correlated with AFM morphological images obtained simultaneously and all converge in revealing the nature (number of layers) of MoS$_2$ flakes. TEPL signal upon deconvolution 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 on to the power of such tip enhanced combinative tool.

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

### Bibliography


