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Identification of Whispering Gallery Mode (WGM) coupled photoluminescence and Raman modes in complex spectra of MoS_2 in Polymethyl methacrylate (PMMA) microspheres

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ABSTRACT

A ripples structure is observed in the photoluminescence (PL) spectra of MoS_2 adsorbed on the surface of single polymethyl methacrylate (PMMA) microspheres in contrast to the broad spectra of nanosheets. Theoretical simulations and photonic nanojet technique have been used to identify the ripple structures. Part of these structures has been found to be due to the whispering gallery modes (WGMs) of the microcavity. The Raman modes of MoS_2 and PMMA, on the other hand, are identified by the photonic nanojet induced enhancement. This work helps applications in photonics and sensing technique which require clean systems with well characterized spectral lines.

1. Introduction

The monolayer molybdenum disulfide (MoS_2) has attracted attention due to its novel optical and electrical properties among the other 2D materials [1,2]. Applications of MoS_2 include solar cells [3], atomically thin p-n junction diodes [4] and photodetectors [5]. Unlike the bulk MoS_2, which is an indirect band gap semiconductor with a band gap of 1.4 eV, monolayer of MoS_2 (hereafter MoS_2) is a direct band gap semiconductor with a band gap of about 1.8 eV [6]. The photoluminescence (PL) of MoS_2 falls in 600–750 nm range [7]. It has been studied from the point of view of strong exciton–photon coupling in tunable optical cavities [8] and as active material in nanolasers [9,10]. Control of spontaneous emission rate of MoS_2 integrated with a photonic crystal microcavity has been demonstrated by Gan et. al [11].

A beam of light incident on the microsphere can undergo multiple total internal reflections to circumnavigate the microcavity. The constructive interference of the beam with itself leads to high quality factor resonances called whispering gallery modes (WGM) [12]. These modes depend on the size of microsphere as well as on the refractive index contrast of the microsphere with its surrounding medium. WGMs find applications as microlaser cavities and optical sensors [13,14]. WGMs are also used in nonlinear optics [15] and QED experiments [16].

In this context, MoS_2 coupled microcavity is an interesting system in the near IR region for WGM related rate modification [17]. In general, overlap of the spectra of coated flourophore with those of the substrate and the microsphere pose limitations. For further studies and applications, distinguishing the spectral lines of the individual components remains an important task in such systems. Therefore, in this paper, after characterization of the MoS_2 nanosheets, we investigate their PL coupled to microspheres by using Raman and luminescence spectroscopy. It is found that the Raman modes of MoS_2 as well as those of PMMA overlap with the WGM peaks. For the clarity in such a complex systems, the observed peaks have been identified (i) theoretically simulating the positions by using the Mie theory and (ii) by enhancing them by more than an order of magnitude using nanojet effect of the microsphere.

2. Experimental

MoS_2 nanosheets dispersed in methanol were purchased from 2D Semiconductors. Poly methyl methacrylate (PMMA) microspheres (MR 10G) were obtained from Soken Kagaku, Japan. For coating, the microspheres where added to MoS_2 nanosheets dispersed in methanol. The dispersion was sonicated for 1 min. This colloidal solution was kept at ambient conditions for 24 h to remove the solvent by evaporation. Dried MoS_2 coated PMMA spheres were transferred to a clean glass slide for the measurements. The absorption spectra of MoS_2 nanosheets dispersed in

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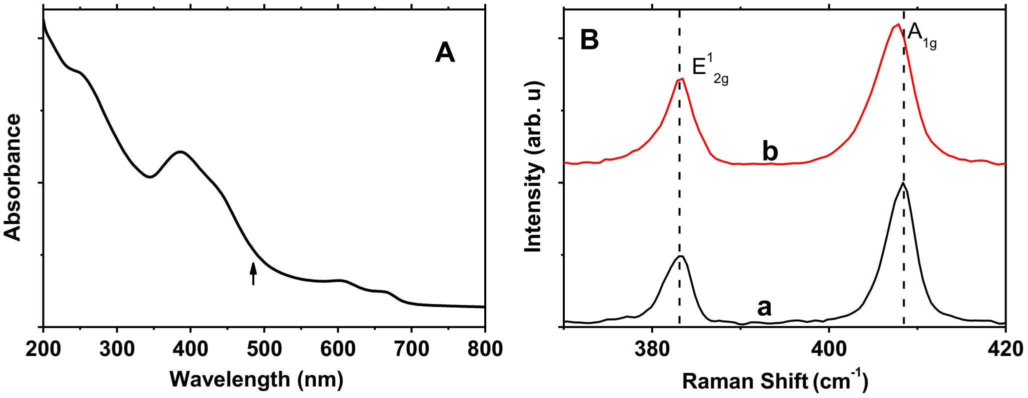

Fig. 1. Absorption spectrum of MoS_2 nanosheets dispersed in methanol (Panel A). The arrow indicates the excitation wavelength used in this work. Panel B gives the Raman spectra of bulk MoS_2 (a) and nanosheets dispersed on Si Substrate (b).

methanol was recorded using the UV-visible dual beam spectrometer (JASCO, V-570). Raman and fluoresce measurement of MoS_2 coated PMMA microspheres were done with a micro Raman spectrometer (Horiba Jobin Yovon LabRAM 800HR) equipped with 488nm laser. Imaging of the nanosheets and energy dispersive x-ray photoelectron spectroscopy (EDAX) were done using JEOL 2100 transmission electron microscope (TEM). Calculations on Mie scattering efficiency was done by Fortran programs of Barber and Hill [9]. A commercial finite element modeling software (Comsol 4.3b) was used to simulate the photonic nanojet. Polydisperse silica microspheres (Duke Scientific) were used for Raman enhancement studies.

3. Theoretical aspects

WGMs are a specific set of eigen solutions of Maxwell's equation of a dielectric microstructures with spherical or cylindrical symmetry. These are characterized by mode number (n) and mode order (l). n is the number of wavelengths of light that fits into the circumference of the microcavity whereas l represents the number of nodes in its radial direction.

Mie theory helps to analyze the WGMs modulated luminescence of flourophores embedded in droplets or microspheres [18]. The scattering efficiency of a microsphere of radius a and refractive index m is given in terms of a_n (TM) and b_n (TE) Mie coefficients as

$$Q_{sca} = \frac{2\pi}{|k|^2} \sum_{n=1}^{\infty} (2n + 1)\left(|a_n|^2 + |b_n|^2 \right) \tag{1}$$

Here k is the wave vector ($2\pi/\lambda$); a_n and b_n are given as

$$a_n = \frac{mj_n(mx)j_n'(x) - j_n'(mx)j_n(x)}{mj_n(mx)H_n^{(1)}(x) - j_n'(mx)H_n^{(1)}(x)} \tag{2.a}$$

$$b_n = \frac{j_n(mx)j_n'(x) - mj_n'(mx)j_n(x)}{j_n(mx)H_n^{(1)}(x) - mj_n'(mx)H_n^{(1)}(x)}. \tag{2.b}$$

where j_n and $H_n^{(1)}$ are the spherical Bessel and Hankel functions and $x = ka$ is known as the size parameter. WGMs occur when denominator in Eqs. (2.a) and (2.b) goes to zero.

4. Results and discussion

4.1. Characterization of the sample

Table 1
Observed peaks and their characteristics in PL and Raman spectra of Bulk and nanosheets.

MoS_2	Peak value (± 0.01 nm)	Stokes' shift[a] (± 0.3 cm^{-1})	Peak intensity (± 0.1)	fwhm (± 0.3 cm^{-1})	Assignment
Bulk	497.29	383.0	48.0	3.60	Raman (E^1_{2g})
	497.91	408.0	100.0	4.21	Raman (A_{1g})
Nanosheet	497.23	380.5	56.3	8.7	Raman (E^1_{2g})
	497.84	405.1	100.0	7.6	Raman (A_{1g})
	500.70	520.6	27.0	7.3	Raman (TO Si)[b]
	523.00	1371.3	17.4	377[c]	PL
	528.00	1552.4	21.8	100[c]	PL
	565.00	2792.7	6.0	617[c]	PL

[a] Stokes' shift from 488 nm.
[b] TO peak of silicon.
[c] By fitting with a Gaussian function.

Fig. 1 (Panel A) shows the absorption spectrum of commercially obtained MoS_2 nanosheets suspended in methanol. It can be seen that the absorption spectrum contains peaks at 254 nm, 387 nm, 442 nm, 607 nm and 664 nm. This spectrum is similar to that reported by Eda et.al. [19].

The Raman spectra of bulk and nanosheets drop casted on a silicon wafer are shown in panel B of Fig. 1. The observed peak positions and their characterization are given in Table 1. For bulk MoS_2, the E^1_{2g} (in-plane vibration of S atoms) and A_{1g} (out of plane vibration of Mo atom) modes were observed at 383 cm^{-1} and 408 cm^{-1} respectively [20]. The full width at half maximum (fwhm) was found to be 3.4 cm^{-1} and 3.6 cm^{-1} respectively. For nanosheets, the Raman modes are observed at 380.5 cm^{-1} and 405.1cm^{-1} with fwhm values of 3.8 cm^{-1} and 4.8 cm^{-1}, respectively. The spacing between E^1_{2g} and A_{1g} mode was found to 24.6 cm^{-1}. This study confirms the few layer nature of the MoS_2 with number of layers as approximately 5 [20,21].

Fig. 2 gives the high resolution TEM image of MoS_2 nanosheets. Besides the lattice structure, the TEM image shows zig-zag edges as well as bends due to defects [22]. EDAX analysis showing the molybdenum and sulfur peaks are also shown in panel C.

The PL spectrum of the few-layer MoS2 drop casted on a silicon wafer was recorded on excitation at 488 nm (Fig. 3). Here the sharp peak with a Stokes' shift of 520.6 cm^{-1} is due to the TO mode of the silicon. It provides the calibration to the spectrum. Apart from the sharp Raman modes of MoS_2 (similar to Fig. 1B), the spectrum has broad peaks with considerable Stokes' shift. The prominent peaks and their fwhms are given in Table 1.

It can be seen that, while the value of Stokes' shift decrease for