Characterization of the Nonlinear Susceptibility of Monolayer MoS₂ using Second- and Third-Harmonic Generation Microscopy

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Abstract:

Second- and third-harmonic generation microscopy of monolayer MoS₂ is reported for imaging and characterization of the material's nonlinearity. A telecommunication wavelength pump is used, revealing the material's promise for use in nonlinear optical devices.

OCIS codes: 160.4236 Nanomaterials, 180.4315 Nonlinear microscopy

1. Introduction

Two-dimensional atomic crystals are emerging as a family of materials with unprecedented optical and electronic properties [1]. Monolayer and few-layer transition metal dichalcogenides, such as molybdenum disulfide (MoS₂), are receiving particular attention following reports of strong photoluminescence, saturable absorption and an indirect-to-direct bandgap transition when approaching the monolayer limit [1, 2]. Leveraging such materials could yield palpable benefits for photonic and optoelectronic devices, although it is first necessary to characterize the optical response of new 2D materials. Here, we measure second-harmonic generation (SHG) and, for the first time, third-harmonic generation (THG) in MoS₂ monolayers, and derive an expression to relate our measurements to the material nonlinear susceptibility by treating a monolayer as a polarization sheet. A telecommunication wavelength is used for the pump, which albeit not being resonant, reveals the high second- and third-order nonlinearity of MoS₂. Comparison with graphene monolayers reveals stronger THG in MoS₂, confirming the potential of MoS₂ for nonlinear photonic devices.

2. Second- and Third-Harmonic Generation Microscopy of Monolayer MoS₂

Monolayer MoS₂ flakes were fabricated by chemical vapor deposition on a silicon (Si) substrate with a ~300 nm silica (SiO₂) coating layer. Our microscope setup enabled linear optical imaging using a green LED source and CCD camera in addition to measurement of harmonics excited by 150 fs pump pulses at 1560 nm from an 89 MHz repetition rate mode-locked Er:fiber laser [Fig. 1(a)-(c)].

Both SHG (at 780 nm) and THG (at 520 nm) were observed, showing the expected quadratic and cubic pump power dependence, respectively [Fig. 1(d)-(e)]. SHG has already been confirmed as a promising technique for imaging MoS₂ and characterizing the second-order nonlinear susceptibility $\chi^{(2)}$ [3–5]. However, the inversion symmetry of even-layered MoS₂ flakes limit this technique to MoS₂ flakes with an odd number of layers [6]. By exploiting a third-order nonlinear effect such as THG, however, samples can be imaged and characterized with any number of layers.

The infinitesimally thin nature of monolayers has raised debate between previous studies regarding the determination of material nonlinear susceptibilities, resulting in reported values varying by many orders of magnitude and prohibiting comparison with other nonlinear materials [3–5]. Here, we treat the problem in the context of surface nonlinear optics following Ref. [3, 7], where interfaces are considered as polarization sheets with distinct dielectric constants and nonlinear polarization to the surrounding materials. By assuming monolayer MoS₂ to behave as a polarization sheet between air and the substrate (also including surface transmission and reflection coefficients to account for the boundary conditions) we find the relationship between pump $I_1(\omega)$ and third-harmonic intensity $I_{\text{THG}}(3\omega)$:

$$I_{\text{THG}}(3\omega) = \frac{1}{\epsilon_0^2} \left[\frac{1}{2c} \left(\frac{2}{1+n_2} \right)^2 \right]^4 (3\omega)^2 |\chi_s^{(3)}|^2 I_1^3(\omega) = \frac{144 |\chi_s^{(3)}|^2 \omega^2}{c^4 \epsilon_0^2 (1+n_2)^8} I_1^3(\omega) \quad (1)$$

Fig. 1. (a) Experimental setup (the second-harmonic was also simultaneously generated, following the same path as the third-harmonic). (b) Optical image and (c) close-up third-harmonic microscope image of monolayer MoS₂. Intensity of (d) second-harmonic and (e) third-harmonic against pump intensity.

where $|\chi_s^{(3)}|$ is the magnitude of the sheet nonlinear susceptibility, ω is the pump frequency, n_2 is the substrate refractive index, and c and ϵ_0 are fundamental constants. Intensity values are related to measured average powers assuming Gaussian-shaped pulses and a Gaussian beam.

From this analysis, we find the third-order sheet polarization to be: $|\chi_s^{(3)}| = 9 \times 10^{-28} \text{ m}^3 \text{ V}^{-2}$. Following a similar derivation for the second harmonic, we compute: $|\chi_s^{(2)}| = 2 \times 10^{-20} \text{ m}^2 \text{ V}^{-1}$. Good agreement is noted with the $|\chi_s^{(2)}|$ value of $\sim 1 \times 10^{-20} \text{ m}^2 \text{ V}^{-1}$ for off-resonant excitation in Ref. [3]. We also repeated our measurements with a graphene monolayer, observing that THG from MoS₂ was ~ 760 times stronger. This suggests a ~ 28 times greater $|\chi^{(3)}|$ response, which in addition to the ability to exhibit second-order nonlinear processes (that are not possible in graphene due to inversion symmetry), suggests that MoS₂ could be a more promising material for nonlinear photonic devices at telecommunication wavelengths.

3. Conclusion

In conclusion, we have measured the magnitude of the second-order and third-order nonlinear susceptibility of monolayer MoS₂ through harmonic generation, demonstrating a stronger third-order response than graphene. Further work is ongoing using MoS₂ flakes with up to 8 layers to quantify the layer-count dependence of the nonlinearity. This characterization paves the way to the development of nonlinear photonic and optoelectronic devices at telecommunication wavelengths which exploit the novel properties of MoS₂.

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