Atom-Dependent Edge-Enhanced Second-Harmonic Generation on MoS$_2$ Monolayers

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**Supporting Information

ABSTRACT: Edge morphology and lattice orientation of single-crystal molybdenum disulfide (MoS$_2$) monolayers, a transition metal dichalcogenide (TMD), possessing a triangular shape with different edges grown by chemical vapor deposition are characterized by atomic force microscopy and transmission electron microscopy. Multiphoton laser scanning microscopy is utilized to study one-dimensional atomic edges of MoS$_2$ monolayers with localized midgap electronic states, which result in greatly enhanced optical second-harmonic generation (SHG). Microscopic S-zigzag edge and S–Mo Klein edge (bare Mo atoms protruding from a S-zigzag edge) terminations and the edge-atom dependent resonance energies can therefore be deduced based on SHG images. Theoretical calculations based on density functional theory clearly explain the lower energy of the S-zigzag edge states compared to the corresponding S–Mo Klein edge states. Characterization of the atomic-scale variation of edge-enhanced SHG is a step forward in this full-optical and high-yield technique of atomic-layer TMDs.

KEYWORDS: MoS$_2$, 2D materials, second-harmonic generation, edge termination, edge states, density functional theory

Nonlinear optical properties of two-dimensional (2D) insulating h-BN,$^4$ semimetallic graphene,$^5$ and semiconducting layered materials such as GaTe$_2$ and MoS$_2$,$^6$ a transition metal dichalcogenide (TMD), have been extensively investigated using multiphoton microscopy. Of these properties, second-harmonic generation (SHG), a second-order optical nonlinearity, is only dipole-allowed in materials without inversion symmetry. This optical method for characterizing 2D materials can be done without any prior processing or harm to the samples on any substrate. In fact, layer number-dependent optical SHG has been discussed using mechanically exfoliated few-layer MoS$_2$. At the exciton resonance energies, the SHG intensity can even be enhanced by up to 3 orders of magnitude.$^7$–$^9$ In addition, SHG from MoS$_2$ bilayers formed by artificial stacking with varying stacking angles allows characterization for the crystal orientation, stacking orientation, uniformity, and domain boundary of TMDs$^{10}$ even over an entire triangular WSe$_2$–MoS$_2$ heterostructure$^{11}$ or in industrial-scale production.$^{12}$ Furthermore, SHG is also applied to device developments such as electrically controlling SHG in monolayer WSe$_2$ transistors for tunable nonlinear optical devices$^{13}$ and deriving the lattice orientation of monolayer MoS$_2$ piezoelectric devices to deposit the electrodes at its zigzag edges.$^{14}$

Second-order optical susceptibilities are highly sensitive to extremely small changes in a material’s electronic states. Recently, one-dimensional (1D) nonlinear optical edge states of a semiconducting MoS$_2$ monolayer have been discovered by Yin et al.$^{15}$ The electronic structural changes at the edges of the MoS$_2$ monolayer result in strong resonant SHG. This phenomenon has been attributed to a two-photon resonance due to the subband transitions from the valence bands to the localized edge states originating from the Mo-zigzag (Mo-zz) edges. These localized midgap states are important because they can affect the optical and transport properties of 2D TMDs.$^{16,17}$ Many kinds of domain shapes of MoS$_2$ monolayers have been synthesized in the chemical vapor deposition (CVD) method, such as triangles, hexagons, truncated triangles, and three-point stars.$^{18}$–$^{20}$ The shape and edge evolution of domains is attributed to the Mo:S ratio, growth temperature, and their influence on the kinetic growth dynamics of

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For monolayer MoS$_2$, the edge structures are commonly believed to be zigzag terminations. However, very recently, bare Mo atoms protruding from a S-zigzag (S-zz) edge, similar to the so-called Klein edge in graphene, have been theoretically predicted and experimentally observed. In this work, the edge morphology and lattice orientation of CVD-grown triangular MoS$_2$ were characterized by atomic force microscopy (AFM) and transmission electron microscopy (TEM), indicating single-crystal monolayers with S-zz or S–Mo Klein edges. Multiphoton laser scanning microscopy is utilized to study 1D atomic edges with localized electronic states, which result in greatly enhanced optical SHG with double resonance peaks and an edge-atom dependent difference in the resonance energy. Density functional theory (DFT) based calculation successfully explains the lower energy of the S-zz edge states in the gap compared to the S–Mo Klein edge states. Multiphoton microscopy is therefore a powerful technique to clarify the atomic-scale variation of edge states in atomic-layer TMDs.

Before demonstrating the SHG properties of 2D MoS$_2$ monolayers, the lattice orientation, edge morphology, and crystallinity of these MoS$_2$ monolayers were characterized. Figure 1 shows the edge structures of CVD-grown triangular MoS$_2$ monolayers on sapphire substrates in different regions (see Supporting Information (SI) for growth procedure and membrane transfer). Looking at the terminations, the AFM...
image of the MoS$_2$ triangle far from the MoO$_3$ precursor has curved edges in Figure 1a.$^{18,20}$ Measuring the height profile of the MoS$_2$ triangle shows that the triangle has a height of \(\sim 0.7\) nm, confirming that it is a monolayer MoS$_2$ (Figure 1b) (see SI Figures S3–S6 for photoluminescence (PL) and Raman spectra). The TEM bright-field image and selected-area electron diffraction (SAED) were used to identify the crystal structure and edge orientation of MoS$_2$ triangles.$^{17}$ The intensity profile can be used to determine which sublattice the edge corresponds to (Figure 1c–e). Four points were selected along a line and the average intensity at each point was measured. The weakest intensity spot is at the second point, which points toward the S sublattice, confirming that the curved edges are S-zz edges. These same measurements were also made on monolayer MoS$_2$ triangles close to the MoO$_3$ precursor whose AFM image shows straight edges (Figure 1f–g).$^{18,20}$ The intensity profile through experimentally measured diffraction points is the same as that from the curved-edge MoS$_2$ triangle (Figure 1h–j). This implies that the MoS$_2$ triangles have the same crystal orientation but have different edges. This edge is temporarily assigned as a S–Mo Klein edge (a S-zz edge with bare Mo atoms).$^{17}$ Because monolayer MoS$_2$ lacks the inversion symmetry that bilayer MoS$_2$ has, it has a strong SHG. Here, an in-house built multiphoton laser scanning microscope (see SI for details) is utilized to study 1D atomic edges with isolated edge-electronic states, which are caused by broken translational invariance at the edge of monolayer MoS$_2$ triangles.$^{15}$ Figure 2a shows SHG images of MoS$_2$ monolayers with S-zz edges as a function of pump wavelength. Looking at the SHG images of MoS$_2$ monolayers over a range of wavelengths, the edges are more enhanced as the pump wavelength approaches the resonant wavelength of the edge states of MoS$_2$. Taking MoS$_2$ monolayers with S-zz edge structures, the enhanced edge SHG is observed at about 1270 nm, becoming less enhanced as the excitation wavelength increases. The edge is enhanced again after 1350 nm (see SI Figure S10 for all pump wavelengths).

To further analyze the enhancement versus wavelength, the ratio of the intensity at the edge of the triangle and the core of the triangle was calculated for each wavelength and compared to previously published results (Figure 2b).$^{15}$ Two resonant peaks are observed, one at \(\sim 1280\) nm (0.97 eV) and one at \(\sim 1380\) nm (0.90 eV). Note that the edge enhancement happens at S-zz MoS$_2$ monolayers, rather than at the Mo-zz observation of ref 15, thus only using an optical microscope to determine the MoS$_2$ edge structure may be unreliable.$^{17}$ The observed small blueshift of the 1280 nm peak compared to the results of ref 15 may be attributed to the compressive strain from sapphire substrates.$^{26}$ Also note that the excitonic effects are important in describing optical properties of excited systems of few-layered MoS$_2$. The two-photon resonances of A and B excitons of the measurements in ref 8 are at 0.94 and 1.05 eV, respectively. These energies are inconsistent with our measurements on the edges. One may expect that the energy position of the excitons could be affected by the edges or grain boundaries and the PL signals could be dominated by the A excitons. Indeed, the MoS$_2$ islands show strong PL intensity variations at the grain boundaries and show 8 and 26 meV blueshifts in the peak energy at the mirror boundary and tilt boundary, respectively.$^{17}$ However, there is no obvious PL contrast observed on monolayer MoS$_2$ edges.$^{15,17}$ At a nanoscale characterization, the PL intensity of the edge within a 300 nm range decreases, but there is no regulated change in its peak energy. Therefore, the excitonic effects should not contribute to the edge-enhanced SHG.

Because the enhanced SHG correlates to the localized edge states, we carry out a set of DFT-based tight-binding calculations and sort out the contribution of edge states to the electronic density of states.$^{15,17,28}$ We start with a full-band tight-binding model for a 2D sheet which contains up to 11 orbital bases (see SI for more details). By tailoring the 2D sheet into 1D ribbons, features of spatial wave function enable us to distinguish between bulk and edge states. The top view of a 2D MoS$_2$ sheet, similar to graphene, is also a honeycomb lattice, except that the zigzag lines here consist of alternating Mo and S atoms. The zigzag ribbons have zigzag lines along the ribbon directions while the finite ribbon width is described by the number of zigzag lines \(N\). In this work, we take \(N = 50\) for the sizable model calculations. The edges could be terminated either by S or Mo atoms. From 2D to 1D, the finite width of the ribbon breaks the translational invariance of the 2D lattice. The primitive cell is therefore \(N\)-times larger. For the case of S (Mo) terminations, the hoppings nearest to the bottom edge are modified to be 1.7 (1.07) times larger in response to the edge relaxation. The calculated 1D subbands and the corresponding density of states are shown in Figure 3 for the
Figure 4. SHG images of (a,b) S−Mo Klein and (c,d) S-zz edge MoS$_2$ monolayers pumped at 1030 and 1270 nm, respectively. Scale bar, 20 μm. (e,f) Intensity profiles measured along the white dotted lines in (a−d). MoS$_2$ with S−Mo Klein edges has edge-enhanced SHG images at 1030 nm but not at 1270 nm. The opposite is observed for S-zz edge MoS$_2$ monolayers. (g,h) SHG images of three-point stars and a curved-edge triangle of monolayer MoS$_2$ with S-zz edges. Scale bar, 5 μm. (i,j) Intensity profiles measured along the white dotted lines in (g,h). The enhanced edge SHG is observed at 1270 nm. A stronger enhanced SHG of the three-point star is due to a greater contribution from edge states. (k) SHG differences can be clearly seen for a truncated triangle. The intensity of the three long sides is stronger than that of the three short sides at 1270 nm. The curved edges of the long sides support a S-zz edge structure. Scale bar, 5 μm. (l) Intensity profiles that are made parallel (line #1) and perpendicular (line #2) to the topmost edge shown in (k). This analysis clearly differentiates between S-zz and Mo-zz edges. The states of Mo-zz edges are out of this energy range, so they are not enhanced. (m) The top view microstructure of the truncated triangle of MoS$_2$ monolayer.

...two different types of edge terminations. The electronic states within the band gap are localized at the edge rather than at the core region. For monolayer MoS$_2$ with S-zz edges, there is a broad peak at about 0.8−0.9 eV in the calculated density of states in Figure 3b. For monolayer MoS$_2$ with S−Mo Klein edges, the edge states are also gapped. The lowest branch of the conducting edge states originates from the S−Mo Klein edge of the ribbon and gives rise to a divergent peak at about 1.2 to 1.3 eV in the density of states in Figure 3d (see SI Figure S8 for details). Theoretical calculations based on density functional theory clearly predict the energy difference between the lower energy of the S-zigzag edge states in the band gap and the higher energy of the S−Mo Klein edge states. At resonance, MoS$_2$ edges experience a two-photon step. In quantum mechanics, when the additional edge-state energy levels are nearly coincident with vacuum transition levels, the second-order optical susceptibilities are strongly enhanced. In the core region of the triangles, there are no additional edge states and no such enhancement is observed. Note that these novel experimental results are not fully matched by our DFT-based calculations, which call for more sophisticated simulations of nonlinear optical properties including interference and excitonic effects in the future.

Using an optical microscope to determine MoS$_2$ edge structures may be unreliable, especially when there is little contrast between MoS$_2$ and the substrate it is grown on, such as sapphire. In order to further explore these phenomena, we imaged the SHG at the edges and cores of the samples at different fundamental wavelengths. As stated above, MoS$_2$ with different edge structures should experience edge enhancement at different wavelengths. Figure 4 compares monolayer MoS$_2$ with S−Mo Klein edges and S-zz edges when pumped at 1030 and 1270 nm. The crystal orientation of S-zz and S−Mo Klein edges was already confirmed to be the same by analyzing the SAED patterns. According to the DFT based calculations above, an energy level above 1 eV was used as a measurement range (see SI Figure S9 for other pump wavelengths). MoS$_2$ with S−Mo Klein edges has edge-enhanced SHG images at 1030 nm, but not at 1270 nm (Figure 4a,b). On the contrary, MoS$_2$ with S-zz edges do not experience edge enhancement at 1030 nm, but at 1270 nm (Figure 4c,d) (see SI Figures S11−S13 for other pump wavelengths). MoS$_2$ edge structures can then be differentiated by their SHG images at specific wavelengths. In order to clearly show the difference, Figure 4e and f are the intensity profiles of the SHG image of S−Mo Klein and S-zz edges MoS$_2$ monolayers pumped at both wavelengths. In addition, the enhancement of the S−Mo Klein edges is observed to be stronger than the enhancement of the S-zz edges because S−Mo Klein edges have a higher density of states. By observing the physical shape of the MoS$_2$ triangles and measuring the changes in their energy, the edge structures have been determined in a faster and more accurate manner and are important for understanding growth dynamics.

During MoS$_2$ growth, if Mo-zz edges grow much faster than S-zz edges in a S-rich environment, the MoS$_2$ monolayer will become a three-point star with S-zz edges (Figure 4g,h). Three-point stars are only a few micrometers wide. When they are pumped at 1030 and 1270 nm, the SHG is only stronger at 1270 nm (Figure 4ij), which agrees with S-zz results. Because the edges of three-point stars make up a larger proportion of the MoS$_2$ sample, the increased SHG intensity is clearer. Considering the more complicated truncated triangle, the SHG image pumped at 1270 nm is shown in Figure 4k. The enhanced SHG is observed at the three long sides but not at the three short sides. Intensity profiles are made parallel and perpendicular to the topmost edge (Figure 4kl). This observation clearly differentiates between S-zz and Mo-zz edges. The states of Mo-zz edges are out of this energy range as predicted by the DFT-based calculation. Thus, it can be inferred that the microstructure resembles Figure 4m. Note that the enhanced SHG observed at the three long sides is not as uniform as in triangles because the samples are still in their...
growth phase. Finally, an atom-dependent edge-enhanced SHG has been thoroughly shown. Further nonlinear optical microscopy research with more complex situations, such as different materials (e.g., WSe₂, MoS₂, WS₂), different structures (e.g., hexagons, six-point stars), defects (e.g., mirror twin and tilt boundaries), and heterostructures (e.g., MoS₂/WS₂/WS₂/MoS₂) can be expected to develop.¹¹,²⁹

In conclusion, multiphoton laser scanning microscopy has been demonstrated on single-crystal triangular MoS₂ monolayers possessing S-zigzag and S–Mo Klein edges grown using CVD. Localized midgap electronic states of the edges could result in greatly enhanced optical SHG even though the edges only consist of a few atoms. Microscopic edge terminations and the edge-atom dependent resonance energies can therefore be deduced based on experimental SHG images, which are further supported by DFT-based calculations. Characterization of the atomic-scale variation of edge-enhanced SHG is a step forward in this full-optical and high-yield technique of atomic-layer TMDs.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.7b04006.

Additional information regarding growth procedure, AFM measurements, TEM sample preparation and measurements, PL and Raman spectroscopy measurements, DFT tight-binding calculations, SHG measurements, and figures (PDF)

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Notes

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