Study of Atom-Dependent Edge-Enhanced Second-Harmonic Generation on MoS_2 Monolayers by Multiphoton Microscopy

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Keywords: MoS_2 monolayers, 2D materials, second-harmonic generation, edge termination, mid-gap states, density functional theory

Nonlinear optical properties of two-dimensional (2D) insulating h-BN [1], semi-metallic graphene [2], and semiconducting layered materials such as GaTe and MoS_2, a transition metal dichalcogenide (TMD) [3], have been extensively investigated using multiphoton microscopy. Of these properties, second-harmonic generation (SHG), a second-order optical nonlinearity, is only allowed in materials without inversion symmetry. Recently, one-dimensional (1D) nonlinear optical edge states of a semiconducting MoS_2 monolayer have been discovered by Yin *et al.* [4]. 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 edges. These localized mid-gap states are important because they can affect the optical and transport properties of 2D TMDs [5]. Many kinds of domain shapes of MoS_2 monolayers have been synthesized in the chemical vapor deposition (CVD) method [6]. 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 edges [6]. For monolayer MoS_2, the edge structures are commonly believed to be zigzag terminations [5,6]. However, very recently, bare Mo atoms protruding from a S-zigzag edge, similar to the so-called Klein edge in graphene, have been theoretically predicted and experimentally observed [7,8]. In this work, edge morphology and lattice orientation of single-crystal MoS_2 monolayers possessing a triangular shape with different edges grown by CVD 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 mid-gap electronic states, which result in greatly enhanced optical SHG. Microscopic S-zigzag edge and S-Mo Klein 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 big step forward in this full-optical and high-yield technique of atomic-layer TMDs.

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