



Summary in English

Optical characterization techniques as ultrasensitive and nondestructive tools, in revealing the influence of local structure on optical properties of two-dimensional semiconducting layers, have emerged widespread attention. In this thesis, nonlinear optical microscopy accompanied by Raman microscopy are used to characterize and understand the structural properties of layered materials, such as structural irregularities, crystalline orientation, and structural symmetry as well as molecular orientation.

Initially, by using confocal scanning optical microscopy coupled with a femtosecond pulsed laser, an efficient second-harmonic generation (SHG) emission at the flake edges of monolayer tungsten disulfide (WS_2) is clearly observed, which is due to the presence of broken translational symmetry and more structural defects at the edges. Interestingly, the room-temperature two-photon induced photoluminescence (2PPL) response shows as the weakest at the flake edges, which exhibits an anticorrelation with SHG signal in the monolayer WS_2 . The obtained results are likely due to the presence of mid-gap electronic states between the valence and conduction bands at the flake edges. In addition, the SHG intensity increases with increasing flake thickness; whilst the 2PPL optical signal is only visible in monolayer WS_2 . The polarization-dependent SHG signal exhibits a six-fold rotational pattern, indicating the three-fold rotational symmetry of WS_2 flake.

Subsequently, the structural irregularities properties of atomically thin molybdenum diselenide ($MoSe_2$) flakes are further investigated by SHG and 2PPL signals. The 2PPL peaks located at ~ 2.30 eV and ~ 2.38 eV could be assigned to the A' exciton and B' exciton transitions of $MoSe_2$ flake, respectively. The crystal orientations of discrete $MoSe_2$ flakes are determined by using the polarized SHG imaging and the angular-dependent SHG spectroscopy. We observed the differences in the angle 3θ which is defined as the angle between the generated SH electric field and the laser electric field, which experimentally

indicates the different crystal orientations of discrete MoSe₂ flakes. Moreover, the bright SHG signal at the grain boundaries and edges is clearly visualized within an individual MoSe₂ flake.

The utilization of confocal microscopy combined with higher order laser modes, Raman enhancement on MoSe₂ flake by using copper phthalocyanine (CuPc) molecules as Raman probe, is demonstrated. Both the photoluminescence and SHG spectroscopies are used to reveal the local structural properties of the MoSe₂ flake. The Raman enhancement on MoSe₂ monolayer at an azimuthally polarized excitation is stronger than the enhancement at a radially polarized excitation. This result indicates that the face-on oriented CuPc molecules can strongly interact with the MoSe₂ monolayer through the ground-state charge-transfer process and the dipole-dipole interaction. Furthermore, the Raman scattering maps on the irregular MoSe₂ surface show a good correlation with the SHG and PL images, suggesting the relationship between local structure and optical properties of MoSe₂ flake.

Eventually, k-space imaging microscopy, in probing the angular emission patterns is implemented based on the confocal microscopy coupled with a femtosecond pulsed laser. The sample location- and thickness-dependent emission patterns of 2PPL signals emanating from single-crystal DH-P-TTA molecule films are demonstrated. Combined with calculated emission pattern, the possible molecular orientation within DH-P-TTA film has been discussed. Two 2PPL peak maxima located at ~516 nm and ~552 nm are distinguished on the film. We observe the anisotropic emission pattern on the ultrathin film, which suggests the molecules adopt a tilt angle and show a high degree of ordering within one domain. Moreover, close correlation between the generated 2PPL signal and the layer thickness of DH-P-TTA film is also demonstrated. The almost isotropic radiative patterns are visualized on the thick films with a thickness of ~33.0 nm and ~58.18 nm, which is attributed to the vertical orientation of DH-P-TTA molecules in the films.