主論文の要約　Summary

Symmetry Engineering of Two-dimensional Materials and Their Transport and Optoelectronic Properties

対称性を制御した二次元物質の光電子物性

ZHANG Shaochun
張　紹春

Since the discovery of graphene, research on two-dimensional (2D) materials has undergone rapid development owing to its unique properties, thus widening the landscape of fundamental research and technological advances. A rich variety of marvelous physical phenomena have been discovered in 2D materials, especially in transition metal dichalcogenides (TMDs) and their heterostructures, such as piezoelectricity, superconductivity and Hall effect, etc. Symmetry in TMDs crystals, including rotational symmetry, mirror symmetry, and inversion symmetry, is essential to determinate their properties. Symmetry breaking in 2D materials play a crucial role in modulating the physical properties.

Meanwhile, the photovoltaic effect (PVE), which emerges in noncentrosymmetric materials, has ignited the search for new PVE

materials. Typically, PVE appears in inhomogeneous semiconductors with p–n junctions, where the spontaneously formed built-in potential generates a photovoltage in response to light irradiation. In contrast, the bulk photovoltaic effect (BPVE), which appears in noncentrosymmetric materials, does not require a built-in potential and is free from the Shockley-Queisser (SQ) limit. TMDs, with low dimensionality, smaller band gap and flexible crystal structure, are a promising class of materials to realize BPVE. In this thesis, we focus on the PVE in TMDs with breaking symmetry.

Chapter 2 reports the symmetry breaking via assembling WS_2/MoS_2 van der Waal heterostructures. Although WS_2 and MoS_2 have C_3 symmetry and sets of mirror planes, the symmetry can probably be altered at WS_2 and MoS_2 interface due to interlayer interaction. Photocurrent mapping measurements have demonstrated that photocurrent up to 28 nA appears without applying bias voltages under 996 μW light excitation, while is almost zero when excitation laser sport is placed outside the stacked region. This work suggests that simply stacking two different layered structures can lead to observing PVE, togethering with the current-voltage (*I-V*) characteristics and power dependence of photocurrent, which is consistent with BPVE.

In chapter 3, we report lifting the inversion symmetry in TMDs by strain. We systematically study the electronic polarization induced by strain, including in-plane and out-of-plane directions. Photovoltaic response in the out-of-plane direction is much stronger than that in the in-plane direction. For observing the out-of-plane photocurrent arising from the out-of-plane polarization, we used a graphene/WS_2/graphene (G/WS_2/G) van der Waals heterostructure, where the top and bottom graphene work as transparent electrodes. In addition, we put a micro-width bar underneath the heterostructure to bend WS_2. Using this structure, ~ 0.339 A/cm^2 photocurrent density at an excitation power of ~ 13.19 W/cm^2 (λ=633 nm) at room temperature was observed, which is very close to the highest photoresponse in low-dimensional system based on BPVE (WS_2 nanotubes).

Chapter 4 reports removing symmetry in MoS_2 by patterning 2D flakes into nanoribbons. MoS_2 nanoribbons along neither the armchair nor zigzag direction were prepared to break the C_3 rational and mirror symmetries simultaneously, and significant photocurrent density can be detected along whole nanoribbons. This study suggests that removing the rational and mirror symmetries by reducing the effective dimensionality from 2D to 1D materials through a simple design can lead to a non-zero PVE. Meanwhile, it provides a simple approach to obtaining materials that exhibit PVE and offers a deeper understanding of symmetry engineering.