

Nano Optical Science Research Section

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1. Introduction

We are working on basic and applied research of nano-materials from a viewpoint of optics and material science. Our research aims at exploring new physical and chemical phenomena leading to applications of novel nano-materials including carbon nanotubes, layered transition metal dichalcogenides, perovskite for efficient utilization of light energy and development of future optoelectronic devices with ultra-low energy consumption. Followings are main research achievements in the year of 2020.

1. Magnetic proximity effect and charge transfer in monolayer semiconductor and double-layered perovskite manganese oxide van der Waals hetero-structure

Recently, monolayer transition metal dichalcogenides (MX_2 : $\text{M}=\text{Mo}, \text{W}$, $\text{X}=\text{S}, \text{Se}, \text{Te}$) have gained increased attention, owing to their novel physical properties and potential applications. The strong confinement and reduced dielectric screening of optically generated electrons and holes in semiconducting monolayer MX_2 enhance Coulomb interaction. Consequently, this imparts an extraordinarily large binding energy to a neutral exciton as a bound electron-hole pair, and to negatively (positively) charged excitons or trions as a bound two electron-hole pair (or an electron and two holes). The excitons and trions in monolayer MX_2 exhibit valley degrees of freedom because the electrons and holes comprising the band-edge located excitons and trions are located at the energy degenerate valleys (K , $-\text{K}$), which are situated at the corners of the hexagonal Brillouin zone. The valley degrees of freedom coupled with the spin degrees of freedom (spin-valley locking), which originate from strong spin-orbit interactions and the breaking of inversion symmetry, enable the selective photogeneration of excitons and trions at the K or $-\text{K}$ valleys by shining circularly polarized light; this leads to the formation of valley-polarized excitons and trions (valley polarization) in monolayer MX_2 .

The optically generated excitons and trions are highly sensitive to the physical properties of substrate materials, owing to the proximity effect. The monolayer MX_2 on the insulating ferromagnetic materials

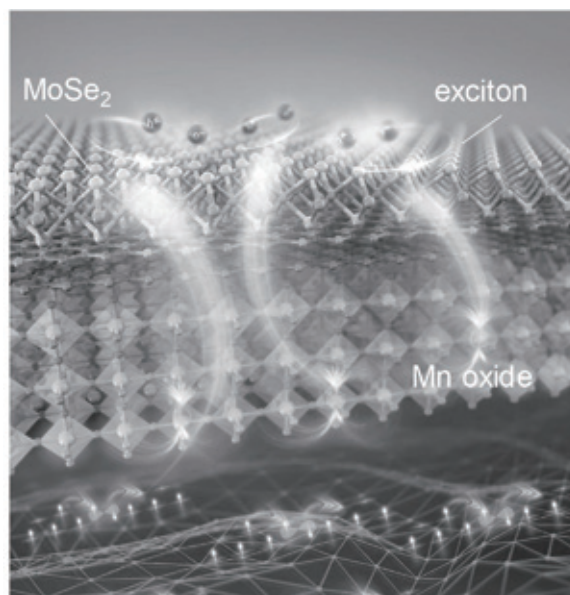


Fig. 1 Schematic of magnetic proximity effect and charge transfer in monolayer MoSe_2 and perovskite manganese oxide in the hetero-structure.

provides a platform for investigating the exchange interactions between the valley spin-polarized excitons (trions) and ferromagnetic spins via proximity magnetic-exchange effects, which leads to tunable valley spin polarization and large valley splitting. The strongly correlated electron system of perovskite manganese oxide has been extensively studied as a model ferromagnetic system for the double-exchange interactions of d -orbital electrons in Mn sites through O $2p$ -orbitals. Numerous novel physical phenomena such as colossal magnetoresistance and charge ordering have emerged in perovskite manganese oxides. The e_g electrons in perovskite Mn oxide trigger the electronic and magnetic phase transition via double-exchange interactions from the paramagnetic insulator phase to the ferromagnetic metal phase at Curie temperature. Even though electronic and magnetic phase transition materials are ideal platforms for creating van der Waals (vdW) heterostructures together with semiconducting 1L- MX_2 , studies regarding the optical physics of these types of vdW heterostructures have not been reported thus far.

Here, we showed the charge transfer and magnetic proximity effect of vdW heterostructures, which

are composed of monolayer MoSe₂ (1L-MoSe₂), few-layer *h*-BN, and double-layered perovskite Mn oxide ((La_{0.8}Nd_{0.2})_{1.2}Sr_{1.8}Mn₂O₇). This vdW heterostructure enabled us to systematically study the interface interactions between the excitonic states (excitons and trions) and magnetic spins as well as charge carriers. We found that the photoluminescence properties of 1L-MoSe₂ strongly depend on the electronic and magnetic properties of the substrate; the charges are transferred from metallic Mn oxide to 1L-MoSe₂, and the valley splitting and polarization are significantly enhanced by introducing a ferromagnetic substrate (Mn oxide), as shown in Figure 1. Moreover, these interactions between 1L-MoSe₂ and Mn oxide can be modulated and controlled by varying the thickness of the few-layer *h*-BN. The vdW structures using electronic and magnetic phase transition materials demonstrated here can provide new opportunities for the modulation and controllability of excitonic states via dielectric screening, charge carriers, and magnetic spins.

2. Inter-valley trion relaxation dynamics in monolayer two-dimensional semiconductor under magnetic field

Novel science and application of valley degree of freedom for information transmission and storage have emerged as valleytronics, which is a new platform for future electronic applications. Monolayer transition metal dichalcogenides 1L-MX₂ as novel two-dimensional (2D) semiconducting materials have attracted tremendous attention for developing valleytronics with coupled spin and valley degrees of freedom. The breaking of Kramers degeneracy due to strong spin-orbit coupling and broken spatial inversion symmetry in 1L-MX₂ produces K or -K valleys at the corner of the hexagonal Brillouin zone that is inequivalent but energy-degenerate. This enables the valley-dependent optical selection rule, in which electrons and holes in a specific valley and spin can be selectively excited by circularly polarized light. The σ^+ and σ^- circularly polarized light can selectively excite the valley-spin polarized excitons (trions) at K and -K valleys. The valley degree of freedom (valley polarization) of excitons (trions) defined as their population difference between K and -K valleys can be monitored through the difference of circularly polarized emission intensity with σ^+ and σ^- component.

The valley polarization of 1L-MX₂ under external field such as electric and magnetic field has been extensively studied from the viewpoints of fundamental valley physics. The breaking of valley degeneracy under the magnetic field because of the broken time-reversal symmetry leads to the photoluminescence (PL) peak splitting of excitons (trions) with σ^+ and σ^- circularly polarized component by Zeeman splitting in 1L-MX₂. Moreover, the valley polarization could be

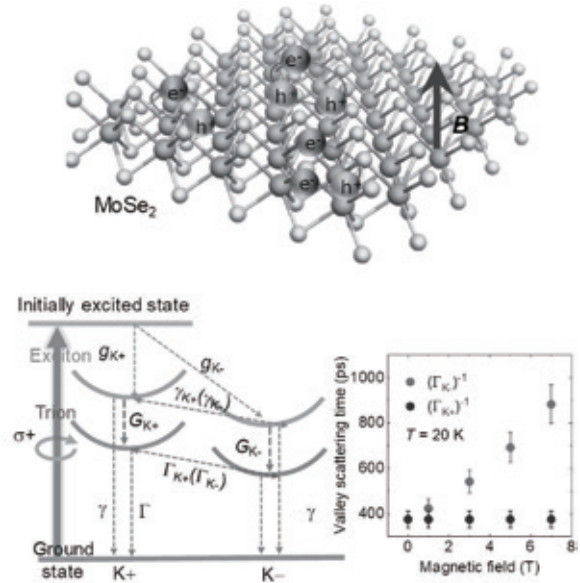


Fig. 2 Schematic of exciton and trion under the magnetic field. Magnetic field induced exciton and trion relaxation dynamics and valley relaxation time under the magnetic field.

modulated by applying magnetic field due to breaking valley degeneracy, where the excitonic valley polarization is dominated by its dynamics: the generation of valley-polarized excitons (trions) and intra-valley and inter-valley relaxation of excitons (trions). The excitonic valley polarization under zero magnetic field in the degenerated valley conditions has been revealed. However, no systematic studies on the dynamics of excitonic valley polarization under magnetic field have been performed. The new insights for the dynamics of excitonic valley polarization show the guides toward long-time keeping and easily controlling of valley polarization, which is strongly required for future valleytronics applications.

In this study, we systematically studied the dynamics of excitonic valley polarization in hexagonal boron nitride (*h*-BN) encapsulated monolayer MoSe₂ (1L-MoSe₂) by polarization- and time-resolved PL spectroscopy under magnetic field. The valley Zeeman splitting induced by an external magnetic field results in the asymmetric valley scattering of trions (excitons) from K to -K valley and vice versa, generating the valley polarization at a finite magnetic field, as shown in Figure 2. To understand the valley dynamics under magnetic field, we build a relaxation model of an exciton and trion including an asymmetric valley scattering rate between K and -K valleys. By solving rate equations obtained from the relaxation model, we described the magnetic field and temperature dependence of the trion valley polarization in 1L-MoSe₂. Our work shows new physical insights for the valley polarization dynamics of excitonic states under magnetic field, which would give a guide to manipulate the valley degree of freedom in valleytronics.

Collaboration Works

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松田一成, 基盤研究(S), 原子層物質におけるバレースピントニクス創生と応用

松田一成, 基盤研究(S), 原子層人工ヘテロ構造におけるバレースピントニクス量子光学の開拓と応用

松田一成, 挑戦的研究(萌芽), 高次データ科学による原子層物質のバレースピントニクス制御

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