<Advanced Energy Conversion Division> Nano Optical Science Research Section

Matsuda, K.; Miyauchi, Y.; Shinokita, K.; Nishihara, T.

Matsuda, K. ...[et al]. <Advanced Energy Conversion Division> Nano Optical Science Research Section. Institute of Advanced Energy, Kyoto University, Annual Report 2021, 2020: 53-56

ISSUE DATE:
2021-03

URL:
http://hdl.handle.net/2433/264012

Advanced Energy Conversion Division

Nano Optical Science Research Section

K. Matsuda, Professor
Y. Miyauchi, Associate Professor
K. Shinokita, Assistant Professor
T. Nishihara, Program-Specific Assistant Professor

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 heterostructure

Recently, monolayer transition metal dichalcogenides (MX$_2$: M=Mo, W, X=S, Se, 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, −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 −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 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 2*p*-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.

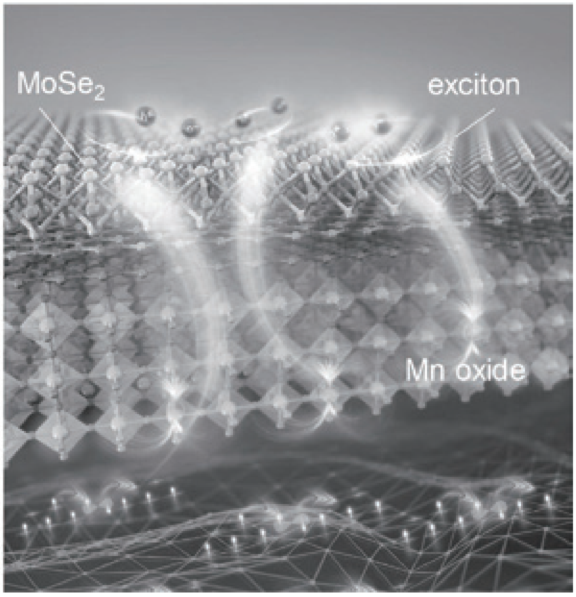

Fig. 1 Schematic of magnetic proximity effect and charge transfer in monolayer MoSe$_2$ and perovskite manganese oxide in the hetero-structure.

Here, we showed the charge transfer and magnetic proximity effect of vdW heterostructures, which are composed of monolayer $MoSe_2$ (1L-$MoSe_2$), few-layer *h*-BN, and double-layered perovskite Mn oxide ($(La_{0.8}Nd_{0.2})_{1.2}Sr_{1.8}Mn_2O_7$). 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-$MoSe_2$ strongly depend on the electronic and magnetic properties of the substrate; the charges are transferred from metallic Mn oxide to 1L-$MoSe_2$, 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-$MoSe_2$ 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-MX_2 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 Krammers degeneracy due to strong spin-orbit coupling and broken spatial inversion symmetry in 1L-MX_2 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 $\sigma+$ and $\sigma-$ 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 $\sigma+$ and $\sigma-$ component.

The valley polarization of 1L-MX_2 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 $\sigma+$ and $\sigma-$ circularly polarized component by Zeeman splitting in 1L-MX_2. Moreover, the valley polarization could be 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.

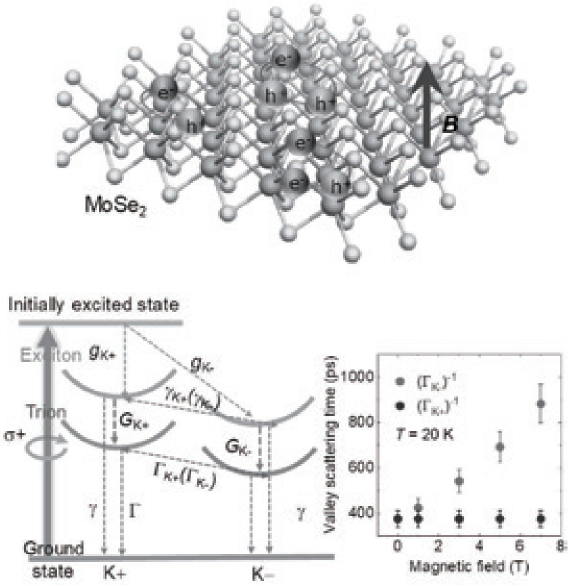

Fig. 2 Schematic of exciton and trion under the magnetic field. Magnetic field induced exciton and trion relaxation dynamics and valley relaxation time under the magnetic field.

In this study, we systematically studied the dynamics of excitonic valley polarization in hexagonal boron nitride (*h*-BN) encapsulated monolayer $MoSe_2$ (1L-$MoSe_2$) 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-$MoSe_2$. 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

松田一成，University of Bordeaux，単一ナノ物質における先端分光

Financial Support

1. Grant-in-Aid for Scientific Research

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

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），高次データー科学による原子層物質のバレースピン制御

宮内雄平，基盤研究(B)，量子物質を用いた非従来型赤外光電変換学理の開拓

篠北啓介，若手研究，二次元遷移金属ダイカルコゲナイドにおけるバレースピン分極の緩和モデルの構築と制御

西原大志，若手研究，熱光エネルギーの高度利用に向けたカーボンナノチューブの熱放射特性の完全解明

2. Others

宮内雄平，科学技術振興機構，原子層ヘテロ構造の光物性・機能開拓

宮内雄平，科学技術振興機構，ナノ物質科学を基盤とするサーモエキシトニクスの創成

Publications

S. Mouri, K. Matsuda, Y. Nanishi, T. Araki, Thermal conductivity of van der Waals hetero-bilayer MoS2/MoSe2, Applied Physics Express, 13, 7, 075001, 2020

Y. Yamada, K. Shinokita, Y. Okajima, S.N Takeda, Y. Matsushita, K. Takei, T. Yoshimura, A. Ashida, N. Fujimura, K. Matsuda, D. Kiriya, Photo-activation of strong photoluminescence in superacid-treated monolayer molybdenum disulfide, ACS Applied Materials & Interfaces, 12, 32, 36496-36504, 2020

S. Zhao, P. Moon, Y. Miyauchi, T. Nishihara, K. Matsuda, M. Koshino, R. Kitaura, Observation of drastic electronic-structure change in a one-dimensional moiré superlattice, Physical Review Letters, 106101, 2020

T. Shiraki, Y. Miyauchi, K. Matsuda, N. Nakashima, Carbon Nanotube Photoluminescence Modulation by Local Chemical and Supramolecular Chemical Functionalization, Accounts of Chemical Research, 53, 9, 1846-1859, 2020

Y. Yamada, K. Shinokita, Y. Okajima, S.N. Takeda, Y. Matsushita, K. Takei, T. Yoshimura, A. Ashida, N. Fujimura, K. Matsuda, D. Kiriya, Photoactivation of Strong Photoluminescence in Superacid-Treated Monolayer Molybdenum Disulfide, ACS Applied Materials & Interfaces, 12, 32, 36496-36504, 2020

Y. Zhang, K. Shinokita, K. Watanabe, T. Taniguchi, Y. Miyauchi, K. Matsuda, Magnetic Field Induced Inter-Valley Trion Dynamics in Monolayer 2D Semiconductor, Advanced Functional Materials, 2006064, 2020

T. Hotta, S. Higuchi, A. Ueda, K. Shinokita, Y. Miyauchi, K. Matsuda, K. Ueno, T. Taniguchi, K. Watanabe, R. Kitaura, Exciton diffusion in hBN-encapsulated monolayer MoSe2, Physical Review B, 102, 11, 115424, 2020

Y. Zhang, K. Shinokita, K. Watanabe, T. Taniguchi, M. Goto, D. Kan, Y. Shimakawa, Y. Moritomo, T. Nishihara, Y. Miyauchi, K. Matsuda, Controllable Magnetic Proximity Effect and Charge Transfer in 2D Semiconductor and Double-layered Perovskite Manganese Oxide van der Waals Heterostructure, Advanced Materials, 32, 2003501, 2020

K. Kato, K. Takaba, S. Maki-Yonekura, N. Mitoma, Y. Nakanishi, T. Nishihara, T. Hatakeyama, T. Kawada, Y. Hijikata, J. Pirillo, L.T. Scott, K. Yonekura, Y. Segawa, K. Itami, Double-Helix Supramolecular Nanofibers Assembled from Negatively Curved Nanographenes, Journal of the American Chemical Society, 2021

F. Yang, S. Wang, P. Dai, L. Chen, A. Wakamiya, K. Matsuda, Progress in recycling organic-inorganic perovskite solar cells for eco-friendly fabrication, Journal of Materials Chemistry A, 9, 5, 2612-2627, 2021

Presentations

松田一成，ナノカーボン・二次元材料の光物性の基礎と応用，フラーレン・ナノチューブ・グラフェン学会，オンライン開催，2020.7.21

宮内雄平，西原大志，カーボンナノチューブの非平衡熱放射と基礎光学関数，ふく射勉強会，オンライイ

ン開催，2020.8.22-23

宮内雄平，カーボンナノチューブ・原子層半導体の新物性開拓，第 3 回超高速光エレクトロニクス研究会，オンライン開催，2020.9.3

Y. Zhang, K. Shinokita, K. Watanabe, T. Taniguchi, Y. Moritomo, Y. Miyauchi, K. Matsuda, Optical properties in van der Waals heterostructure of monolayer MoSe2 and perovskite manganese oxide, 第 81 回応用物理学会秋季学術講演会, オンライン開催, 2020.9.8

W. Zhang, K. Tanaka, Y. Hasegawa, K. Shinokita, K. Matsuda, Y. Miyauchi, Chemically brightened and highly valley polarized trions in monolayer MoS2, 第 81 回応用物理学会秋季学術講演会，オンライン開催，2020.9.8

西原大志，ナノカーボン物質の励起子光物性研究，日本物理学会，オンライン開催，2020.9.9

松田一成，二次元物質と集積構造の光科学，応用物理学会，オンライン開催，2020.9.10

田中絢也，八谷健吾，張文金，松田一成，宮内雄平，機械学習解析による二次元半導体の局所バレー分極決定要因の特定，第 81 回応用物理学会秋季学術講演会，オンライン開催，2020.9.10

松田一成，ナノカーボン・原子層物質の光物性の基礎と応用，フラーレン・ナノチューブ・グラフェン学会，オンライン開催，2020.9.16

篠北啓介，王暁凡，宮内雄平，松田一成，単層 WSe2 におけるバレー内緩和ダイナミクス，日本物理学会 2020 秋季大会，オンライン開催，2020.9.16-18

西原大志，髙倉章，松田一成，田中丈士，片浦弘道，宮内雄平，単一構造カーボンナノチューブ薄膜の広帯域複素屈折率スペクトル，フラーレン・ナノチューブ・グラフェン学会，オンライン開催，2020.9.18

Y. Zhang, K. Shinokita, Y. Miyauchi, K. Matsuda, Charge transfer and magnetic proximity effect in van der Waals heterostructure of monolayer MoSe2 and double-layered manganese oxide, A3 ワークショップ, Online, 2020.9.24

篠北啓介，原子層半導体の moiré 光科学，第 12 回 K-CONNEX 研究会，京都大学吉田キャンパス学術研究支援等地下一階会議室，2020.10.9

西原大志，カーボンナノチューブの熱励起子輻射の研究，分子研研究会，オンライン開催，2020.12.4

K. Shinokita, Resonant excitation of moiré exciton in a WSe2/MoSe2 heterobilayer, The 7th International Workshop on 2D Materials, Online, 2021.2.18-19

Y. Zhang, K. Shinokita, Y. Miyauchi, K. Matsuda, Intralayer exicitons trapped in moiré potential on monolayer-MoSe2/NiPS3 heterostructure, 第 60 回フラーレン・ナノチューブ・グラフェン総合シンポジウム, Online, 2021.3.2

篠北啓介，宮内雄平，松田一成，WSe2/MoSe2 ヘテロ二層におけるモアレ励起子の励起発光分光，日本物理学会第 76 回年次大会，オンライン開催，2021.3.12-15

宮内雄平，カーボンナノチューブの熱光物性と太陽エネルギー変換応用，日本化学会 第 101 春季年会 (2021)，オンライン開催，2021.3.22