Tuesday Posters

FLATLANDS

beyond graphene

2019 Toulouse

Poster-Tu01

Correlating the Structure of 2D Materials with Their Catalytic Activity

Maya Bar Sadan[1]

[1]*Department of Chemistry, Ben Gurion University, Beer sheva, Israel*

The ability to dope them by substituting with various transition metals make transition metals dichalcogenides (TMDs) an interesting system for tailor-made applications. Here, the formation of ternary compounds of TMDs by wet chemistry will be described. Specifically, the doping of TMDs with other transition metals and the impact it has on their catalytic properties for hydrogen production will be presented. The growth mechanism of nanoflowers nanostructures of TMDs was revealed using electron tomography. This growth mechanism allows for facile doping of the materials by adding the dopants either at the beginning or at the end of the reaction, thus forming a homogenous material or a graded one. We have used this approach to dope MoS_2 and WSe_2 with Ru, Co, Fe, Ni and significantly improved their catalytic activity towards hydrogen production.

In addition, we have surveyed the structural features of various hybrids in order to correlate them with the catalytic activity. Typical defect motifs will be shown and discussed. This work aims at correlating the atomic-scale structures with the catalytic activity, and for that goal to be achieved, there is a need to understand the dopant sites and the atomic scale arrangement within the MoS_2 lattice. The use of high-resolution electron microscopy with other characterization methods allows first the understanding of the structural features of the materials and thereafter it will serve to understand the origin of catalytic activity.

FIG. 1. Functional materials based on TMDs are produced by using various synthetic routes

Poster-Tu02

Heterojunctions in two-dimensional indium selenide nanosheets

D. Andrés-Penares,[1] M. Brotons-Gisbert,[1] A. Molina-Sánchez,[1] J. Avila,[2] M.C. Asensio,[3] J. P. Martínez-Pastor,[1] J.F. Sánchez-Royo[1]

[1]*Materials Science Institute of the University of Valencia(ICMUV), P.O. Box 22085, 46071 Valencia, Spain*
[2]*SOLEIL Synchrotron, Saint Aubin, BP 48, 91192 Gif-sur-Yvette, France*
[3]*Materials Science Institute of Madrid (ICMM-CSIC), 28049 Cantoblanco, Spain*

Following the route path marked by graphene, many others layered materials have managed to be exfoliated until the single-layer unit, these exhibiting a distinctive semiconducting behaviour [1-5]. These two-dimensional semiconductors can constitute the building blocks of new heterostructures based on 2D materials [6] with potential applications in optoelectronic [7], spintronic [8,9] and valleytronics [10,11].

The fabrication of 2D heterostructures with clean and sharp interfaces is essential for preserving optoelectronic properties driven by the interlayer or intralayer coupling [12]. Van der Waals heterostructures could be created by stacking diferent 2D materials using mechanical transfer techniques [13]. However, the control of the interface quality remains challenging. Only under controlled interface conditions, abrupt interfaces have been realized and allowed, for instance, the realization of interlayer excitonic states in van der Waals bound heterobilayers [14]. In this work, we show that the particular and distinct properties of two-dimensional indium selenide nanosheets can open the door for the development of new heterjunctions and related devices. In particular, we have analysed the electronic properties of interfaces formed in multi-terraced InSe nanosheets, by nano-photoemission and photocurrent response measurements, demonstrating that abrupt interfaces naturally appear in multi-terraced nanosheets of 2D InSe which can be used for the fabrication of planar devices based on this 2D semiconductor.

[1] H. Zeng, et al., Nat. Nanotechnol. **7**, 490 (2012).
[2] X. Xu, et al., Nat. Phys. **10**, 343 (2014).
[3] G. W. Mudd, et al., Adv. Mater. **25**, 5714 (2013).
[4] J. F. Sánchez-Royo, et al., Nano Res. **7**, 1556 (2014).
[5] M. Brotons-Gisbert, et al., Nano Lett. **16**, 3221 (2016).
[6] T. Niu, et al., Prog. Surf. Sci. **90**, 21 (2015).
[7] X. Li, et al., Appl. Phys. Rev. **4**, 021306 (2017).
[8] K. F. Mak, et al., Science **344**, 1489 (2014).
[9] Y.-J. Chen, et al., Nat. Photonics **11**, 431 (2017).
[10] N. Zibouche, et al., Ann. Phys. **526**, 395 (2014).
[11] W. Han, APL Mater. **4**, 032401 (2016).
[12] A. K. Geim, et al., Nature **499**, 419 (2013).
[13] Y. Gong, et al., Nat. Mater. **13**, 1135 (2014).
[14] P. Rivera, et al., Nat. Comm. **6**, 7242 (2015).

Poster-Tu03

Improving stability of perovskite solar cells using two-dimensional transition metal dichalcogenides

Meiying Liang,[1] Adnan Ali,[2] Abdelhak Belaidi,[2] Fadwa EI-Mellouhi,[2] and Valeria Nicolosi[1]

[1]School of Chemistry and CRANN, Trinity College Dublin, Ireland

[2]Qatar Environment and Energy Research Institution, Hamad Bin Khalifa University, Qatar

High-performance, economically viable, large-scale producing and rich resources are the key to developing novel solar cell materials. Perovskite solar cells (PSCs) are one of the most promising candidate as the next generation solar cell technology.[1] However, the stability has become a main barrier for further development compared to silicon-based solar cells on the market.[2] Perovskites are very sensitive to environment such as air, UV light, water, thermal stress and other factors.[2] These stressors-induced degradation can be effectively reduced by inserting a buffer layer into the device structure.[2]

Based on the large number of studies, there is no doubt that two-dimensional (2D) transition metal dichalcogenides (TMDs) semiconductors represent one of the most promising materials for photovoltaic devices due to their high carrier mobility, high transparency, tunable band gap, low cost, and solution-processable properties.[3] Besides, it is reported that the ultrafast and efficient charge transfer were detected in the perovskite-TMDs heterostructures.[4] Therefore, combination of perovskite and 2D TMDs gives us opportunity to obtain solar cell devices with improved PV performance such as higher efficiency and longer-term stability.

In this work, 2D TMDs (such as MoS_2, $MoSe_2$, etc.) nanosheets were prepared *via* the sonication-assisted liquid phase exfoliation (LPE) method. This method is non-destructive, insensitive to air and water. Besides, these are processed from the liquid phase so that solar cell devices may be produced at large scale with low cost and a simple process. Then, these exfoliated 2D TMDs were used as a buffer layer of PSCs. Compared to the standard PSC, the stability of the PSC adding a 2D TMDs buffer layer improved apparently. As shown in FIG 1, PCE of the standard PSC decreased 58.4 % from initial, however, PCE of the PSC with a 2D TMDs buffer layer only decease 12.2 % after 1 h. In addition, the PSC using a 2D TMDs buffer layer still can maintain over 16% of PCE. Our results open the new window for developing PSCs to realize the commercialization in the future.
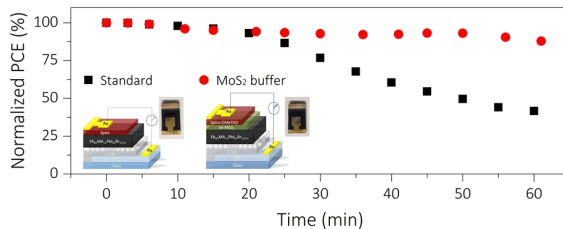

FIG. 1. Comparison of the stability of standard PSC and the PSC with a MoS_2 buffer layer.

[1] H. J. Snaith et al. Nature, 501, 395, (2013)

[2] Gon Namkoong et al. Appl. Sci., 9, 188, (2019)

[3] Francesco Bonaccorso et al. Adv. Energy Mater. 6, 1600920, (2016)

[4] Yangfeng Zhang et al. J. Phys. Chem. Lett.,9, 1655 (2018)

Understanding the Role of Precursors on the Final MoSe$_2$ Product: Correlating the Growth Mechanism and the Catalytic Activity for the Hydrogen Evolution Reaction

S. Kolatker[a], R. Bar-Ziv[b] and M. Bar-Sadan[*a]

[a] Ben-Gurion University of the Negev, Department of Chemistry, Beer-Sheva, Israel.
 E-mail: barsadan@bgu.ac.il
[b] Nuclear Research Center Negev, Beer-Sheva 84190, Israel.

Nanoflowers have unique morphology of exposed edges that is one of the most promising morphologies for catalysis [1]. Modifying the synthesis of MoSe$_2$ can change properties such as morphology, crystallinity, average particle size and catalytic activity. In this project 3 different synthesis protocols were used in order to study the correlation between different precursors and the final morphology and the resulting effect on the catalytic performance of HER. The protocols included the following precursors combinations: I) Na$_2$MoO$_4\cdot$2H$_2$O/ ODE-Se, II) MoO$_2$(acac)$_2$/ ODE-Se, and III) MoO$_2$(acac)$_2$/ DBDSe. Moreover, additional parameters such as the feed ratio between Se and Mo and the reaction duration were varied in order to systematically study the effect of crystallinity and stoichiometry over the catalytic performance towards the HER. The characterized samples show connection between reaction time and average size of particles and crystallinity. Not all precursors combinations resulted in the nanoflower structure. The combination that showed the best results is Na$_2$MoO$_4\cdot$2H$_2$O/ODE-Se where the particles are bigger than the other two precursors combination. The Na$_2$MoO$_4\cdot$2H$_2$O/ODE-Se exhibit low Tafel slope values (54-68 mV/dec) and low overpotentials of 0.221-0.245 mV. In this project, various MoSe$_2$ structures were produced and fully characterized to gain insights into the growth mechanism and the final products' applicability to serve as HER catalysts.

Reference:

1.   Meiron, O.E., L. Houben, and M. Bar-Sadan, *Understanding the formation mechanism and the 3D structure of Mo(S$_x$Se$_{1-x}$)$_2$ nanoflowers.* RSC Advances, 2015. **5**(107): p. 88108-88114.

Poster-Tu05

In-situ Doping of Black Phosphorus for Potential Applications

Nikolas Antonatos,[1] Seyyed Mohsen Beladi-Mousavi,[2] Daniel Bouša,[1] Svyatoslav Shcheka,[3] Martin Pumera,[2] and Zdeněk Sofer,[1]

[1] *Department of Inorganic Chemistry, University of Chemistry and Technology Prague, Technická 5, 166 28 Prague 6, Czech Republic*

[2] *Center for Advanced Functional Nanorobots, Department of Inorganic Chemistry, University of Chemistry and Technology Prague, Technická 5, 166 28 Prague 6, Czech Republic*

[3] *Bayerisches Geoinstitut (BGI), Universität Bayreuth, Universtätstrasse 30, 95447 Bayreuth, Germany*

Black phosphorus (BP) is a two-dimensional semiconductor with promising properties for catalysis, energy storage and conversion as well as electronic device applications but nevertheless control of its electronic structure is critical for such applications. However, the biggest drawback to the application of black phosphorus is the low stability of the material under ambient conditions since BP reacts with oxygen on the surface. It has been predicted that doping black phosphorus with proper elements is a promising method to effectively suppress the ambient degradation of black phosphorus. [1] Substitutional doping of phosphorus by electron donating (e.g. sulfur) or electron accepting elements (e.g. germanium) can significantly change its properties, especially charge carrier concentration. [2] Thus, by selectively doping BP may result in implementing this promising material in future applications.

It is presented here the in-situ doping of black phosphorus by its direct synthesis from a mixture of red phosphorus and dopant by high pressure synthesis. In detail, the incorporation of germanium, sulfur, selenium and tellurium within black phosphorus was examined where significant differences in incorporation of individual elements was observed. SEM images revealed the bulk state of all the materials with evident well-layered stacked arrangements, while the elemental maps of EDS exposed uniform distribution of tellurium and sulphur within the phosphorus, however concentration of the latter is close to the detection limit and local accumulation could be observed for germanium and selenium. The XRD patterns of the doped BP materials were almost identical to the respective one of pure BP confirming the high crystallinity of the materials and indicating no significant changes in the crystallinity or the interlayer distance of the materials after doping. In the Raman spectra the three characteristic vibrational modes of BP were observed in all materials. For the doped materials, these vibrational modes were shifted towards lower wavenumbers which was attributed to doping-induced changes in thickness of the BP puckered layers and the spacing between them.

Fundamental electrochemical properties of the synthesized materials were tested by investigating the heterogenous electron transfer of three redox couples: Ruthenium hexamine ($[Ru(NH_3)_6]^{2+/3+}$), ferro/ferricyanide ($[Fe(CN)_6]^{4-/3-}$) and hydroquinone. Notably, for the ruthenium hexamine redox couple, (FIG. 1) the ΔE value of GC is almost equal to the pure and doped BP exhibiting a comparable HET which indicates the excellent electronic properties of the bare and doped BP-modified electrodes.
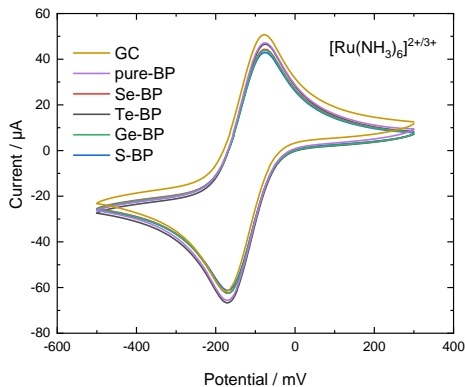

FIG. 1. Cyclic voltammpgram (vs. Ag/AgCl) of bare glassy carbon (GC) compared with pure and doped black phosphorus modified GC in $Ru[(NH_3)_6]^{2+/3+}$ redox couples (10 mM), scan rate: 100 mV s^{-1}.

[1] Yang, B., Wan, B., Zhou, Q., Wang, Y., Hu, W., Lv, W., Chen, Q., Zeng, Z., Wen, F., Xiang, J., Yuan, S., Wang, J., Zhang, B., Wang, W., Zhang, J., Xu, B., Zhao, Z., Tian, Y., Liu, Z., *Adv. Mater.,* **2016,** *28,* 9408

[2] Kim., J., Baik, S.S., Ryu, S.H., Sohn, Y., Park, S., Park, B.-G., Denlinger, J., Yi, Y., Choi, H.J., Kim, K.S., *Science,* **2015,** *349,* 723

Poster-Tu06

Substitutional Metal doping Effect of M-WSe2 (M= Fe, Co, Nb, Ni, Zr) Catalyst for Electrochemical Hydrogen Evolution Reaction

Sunil R. Kadam,[ab] Ronen Bar-Ziv,[abc] Maya Bar-Sadan,[ab*]

[a]Ben-Gurion University of the Negev, Department of Chemistry, Beer-Sheva, Israel.

[b]Ilse Katz Institute for Nanoscale Science and Technology, Ben Gurion University, Beer Sheva Israel.

[c]Nuclear Research Center (NRCN), Beer Sheva, Israel.

Constructing Nickel-doped tungsten selenide (Ni-WSe$_2$) is promising electrocatalyst to build high-performance and low cost electrochemical hydrogen evolution reaction. Here, we report the synthesis of some transition metal (M= Fe, Co, Nb, Ni, Zr) doping in WSe$_2$ for the first time with abundant active sites available for the catalytic activity. Among the M-doped catalyst, Ni-WSe$_2$ is promising electrocatalyst to build high-performance and low cost electrochemical hydrogen evolution reaction. The controlled synthesis of Ni-doped nanostructures, with feed ratios of 3%, 5% and 10% Ni, maintained similar morphology, offering an opportunity to study the effect of Ni doping on the catalytic activity. The 10 % Ni-doped WSe$_2$ exhibits a significantly improved HER performance with over potential at -10 mA cm^{-2} of -259 mV and Tafel slope 86 mV dec^{-1} was much better than reported for pristine and doped WSe$_2$ sample. Thus, Ni-WSe$_2$ possesses the smallest resistance, which contributed to the facilitated faster catalytic reaction. Such structures can be designed and implemented in other transition metal dichalcogenide based materials for electrochemical and other applications.
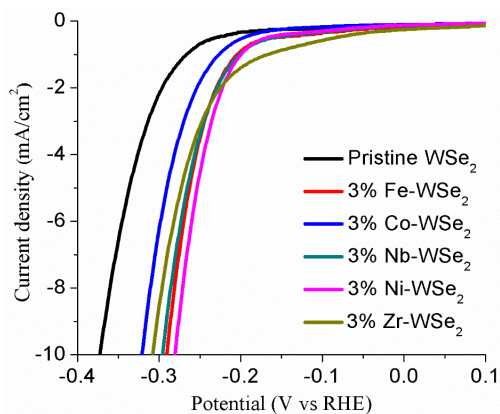
FIG. 1. (a) HER polarization curves of the pristine WSe$_2$ along with 3 % Fe, Co, Nb, Zr and Ni-doped WSe$_2$ sample in 0.5 M H$_2$SO$_4$.

Reference

1.   Lu, Z., et al., Adv. Mater., 2014, 26(17), 2683-2687.

2.   Meiron, O.E., et al., Nanoscale, 2017. 9(37),13998-14005.

3.   Dai, X., et al., ACS Appl. Mater. Interfaces, 2015. 7(49), 27242-27253.

Poster-Tu07

Theory of Coherent Pump-Probe Signatures in Single-Layer Transition Metal Dichalcogenides

Florian Katsch,[1] Malte Selig,[1] and Andreas Knorr[1]

[1]*Institut für Theoretische Physik, Nichtlineare Optik und Quantenelektronik,
Technische Universität Berlin, 10623 Berlin, Germany*

Valley-selective circular dichroism, strong Coulomb and light-matter interactions in monolayer transition metal dichalcogenides (TMDCs) along with intervalley interactions allow to study new many-body physics in these atomically thin materials. Moreover, the possibility to selective excite separate spin-split bands and distinguished corners of the hexagonal Brillouin zone at the same time may lead to future spin- and valley-tronics applications. In order to describe the optical response of single-layer TMDCs a microscopic theory based on tightly bound electron-hole pairs, referred to as excitons, is developed [1, 2]. The presented approach not only incorporates Hartree–Fock effects but also accounts for higher-order correlations such as biexcitons and the unbound exciton-exciton scattering continua [3-6], cf. Fig. 1, as well as different intra- and intervalley couplings.
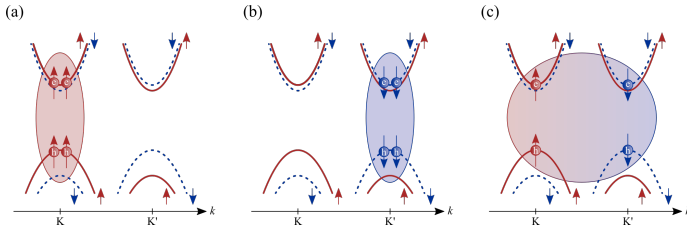

FIG. 1.   *Schematic illustration of intra- (a,b) and intervalley (c,d) four-particle correlations giving rise to intra- and intervalley coupling. The spins of incorporated electrons and holes are (a,d) either identical or (c,b) the involved carriers are associated with different spin-split valence and conduction bands.*

The presented theory is used to theoretically model exciton-dominated pump-probe experiments in the coherent limit and unravels the signatures of the different processes contributing to intra- and intervalley coupling [7]. It is shown that the inclusion of bound biexcitons and unbound exciton-exciton scattering continua, apart from strongly off-resonant Hartree-Fock effects [8], leads to an ultrafast intravalley mixing of A−B excitons and intervalley mixing of A−A' as well as A−B' excitons, cf. Fig. 2.
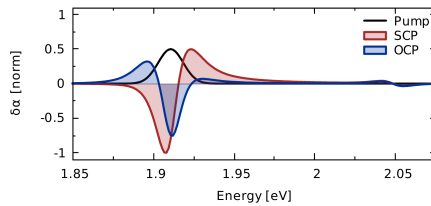

FIG. 2.   *Numerical simulation of differential absorption for MoS_2 on a SiO_2 substrate for pumping an probing with light of same (SCP) and opposite (OCP) circular polarization. The excitation pulse is shown black.*

[1] A. L. Ivanov and H. Haug, *Phys. Rev. B* **48**, 1490 (1993).
[2] F. Katsch et al., *Phys. Stat. Sol. B*, 1800185 (2018).
[3] V. M. Axt and A. Stahl, *Z. Phys. B* **93**, 2 (1994).
[4] R. Takayama et al., *Eur. Phys. J. B* **25**, 445 (2002).
[5] S. Schumacher et al, *Phys. Rev. B* **73**, 035318 (2006).
[6] A. Steinhoff et al., *Nat. Phys.* **14**, 1199 (2018).
[7] C. Mai et al., *Nano Lett.* **14**, 202 (2013).
[8] R. Schmidt et at., *Nano Lett.* **16**, 2945 (2016).

Poster-Tu08

Raman spectroscopy on MoSe$_2$-WSe$_2$ heterostructures

Sebastian Meier,[1] Matthias Dietl,[1] Johannes Holler,[1] Michael Kempf,[1] Tobias Korn,[2] and Christian Schüller[1]

[1]*Institut für Experimentelle und Angewandte Physik,*
Universität Regensburg, D-93040 Regensburg, Germany

[2]*Institut für Physik, Universität Rostock, D-18059 Rostock, Germany*

We perform resonant Raman scattering to look for electronic excitations in MoSe$_2$. In our microscope setup we use a Ti:Sapphire laser and a triple Raman spectrometer, which allows us to tune the excitation energy across the optical bandgap. The sample is placed inside a cold-finger cryostat and cooled down to T=4 K. As the strong photoluminescence of MoSe$_2$ monolayers at low temperatures complicates the detection of Raman lines under resonant excitation, we use a MoSe$_2$-WSe$_2$ heterostructure (Fig. 1a). In this heterosturcture, the photoexcited charge carriers are separated into the constituent layers and form interlayer excitons, which are at lower energies than the intralayer excitons of the individual layers. The intralayer photoluminescence is therefore strongly quenched, allowing resonant Raman measurements.

Tuning the excitation energy across the optical transitions of MoSe$_2$, we observe a low energy Raman excitation which is visible in resonance to the trion energy, only (Fig. 1b). Since we can not interpret this peak by scattering of phonons, we propose a double resonance process, where in the inelastic scattering process a singlet trion is excited into a triplet trion by an intervalley spinflip transition of electrons.
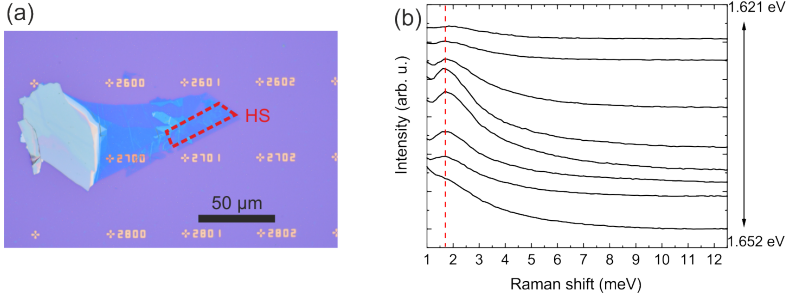

FIG. 1. (a) MoSe$_2$-WSe$_2$ heterostructure (marked as "HS") produced by mechanical exfoliation. (b) Raman spectrum of the heterostructure for varying laser energies. In resonance to the trion of MoSe$_2$, a low energy peak appears (marked by dashed line).

Hybrid Nanostructures of Ag NPs@MoS$_2$ and Cu NPs@MoS$_2$ – Growth Mechanism and Catalytic Activity Towards the Hydrogen Evolution Reaction

Avi Bar-Hen[1,2,3], Ronen Bar Ziv[3], Simon Hettler[4], Raul Arenal,[4,5,6] and Maya Bar Sadan*[1,2]

[1] Department of Chemistry, Ben-Gurion University of the Negev, Beer-Sheva-8410501, Israel
[2] Ilse Katz Institute for Nanoscale Science and Technology, Ben-Gurion University of the Negev, Beer-Sheva-8410501, Israel
[3] Nuclear Research Center Negev, Beer-Sheva, Israel
4. Laboratorio de Microscopías Avanzadas, Instituto de Nanociencia de Aragón, Universidad de Zaragoza, 50018 Zaragoza, Spain
5. ARAID Foundation, 50018 Zaragoza, Spain.
6. Instituto de Ciencias de Materiales de Aragon, CSIC-U. de Zaragoza, Calle Pedro Cerbuna 12, 50009 Zaragoza, Spain
* barsadan@bgu.ac.il

The development of electrocatalysts based on metal NPs and semiconductors for the hydrogen evolution reaction (HER) holds significant promise to a spectrum of energy conversion technologies. MoS$_2$ is a promising candidate for electrochemical hydrogen production due to its high activity and stability. However, the efficiency of hydrogen production by MoS$_2$ is limited by the number of active sites, e.g. edges, which can be improved by changing the morphology or combining MoS$_2$ with other materials to get the surface more catalytically active. Here we show the preparation, characterization and catalytic activity towards HER of Ag NPs@MoS$_2$ or Cu NPs@MoS$_2$ hybrid nanostructures. Understanding the dual effect of the metal NPs over MoS$_2$ can shed light over the catalytic mechanism of this system and can have a rich platform for designing a new well improved based-semiconductor-metal NPs catalyst for HER. We show the nature of the bonding of metal NPs and MoS$_2$. TEM images of Ag NPs@MoS$_2$ and Cu NPs@MoS$_2$ present nanostructured metal NPs (50 nm in average) wrapped with multi-layers of MoS$_2$. The formation of non-crystalline MoS$_2$ around the metal NPs is proved by XPS and XRD analysis. High-resolution transmission electron microscopy of the hybrid provides direct evidence of the core–shell morphology. The initial attachment of MoS$_4^{2-}$ to the metal NPs during the synthesis and after the thermal treatment, is also analyzed by XPS. Electrochemical measurements show that the hybrids' catalytic activity towards HER is better than the sole MoS$_2$ or Ag/Cu NPs. The large enhancement in the catalytic activity can be attributed to the synergistic effect of charge transfer to the MoS$_2$ and a morphological effect in which more active sites are exposed due to the curvature of MoS$_2$ around the NPs.
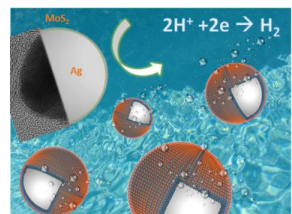
Poster-Tu10

Probing spin-valley polarization dynamics in MoSe$_2$/WSe$_2$ heterostructures

Michael Kempf,[1] Florian Raab,[1] Markus Schwemmer,[1] Andreas Hanninger,[1] Philipp Nagler,[1] Christian Schueller,[1] and Tobias Korn[2]

[1]*Regensburg University, 93053 Regensburg, Germany*

[2]*Rostock University, 18051 Rostock, Germany*

Transition metal dichalcogenides (TMDC) have revealed many intriguing properties in recent years. For valleytronics especially, the coupling of spin and valley degree of freedom shows great promise. Combined with valley-selective optical selection rules, a chosen spin polarization can easily be introduced into these systems. Keeping possible future applications in mind, a long spin polarization lifetime is of great importance, yet in pristine monolayer TMDC this is strongly limited due to ultrafast exciton recombination and electron-hole exchange[1].

Through two-color time-resolved Kerr rotation and ellipticity measurements we are able to study the spin-valley dynamics in n-doped MoSe$_2$ and compare it to the undoped case. Here we observe a drastic lifetime increase from the order of picoseconds to nanoseconds[Fig.1], significantly exceeding the lifetimes of excitons and trions. This can be attributed to a transfer of spin polarization to resident carriers[2]. Following a similar reasoning we investigate two-dimensional MoSe$_2$/WSe$_2$ heterostructures, where through a typ II band alignment electrons and holes are spatially separated. This in turn suppresses their recombination as well as exchange interaction thus leading to an increase of spin polarization lifetime.
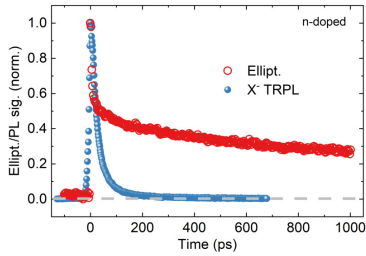

FIG. 1. *Time-resolved ellipticity and trion photoluminescence measurements of n-doped MoSe$_2$ monolayer[1].*

[1]M. Glazov *et al.* PRB **89**, 201302(R) (2014).
[2]M. Schwemmer *et al.* Appl. Phys. Lett. **111**, 082404 (2017).

Poster-Tu11

Relation between topology and electronic structure of 2D polymers

Maximilian A. Springer,[1] Agnieszka B. Kuc,[1] Thomas Heine,[1,2]

[1]*Helmholtz-Zentrum Dresden-Rossendorf, Forschungsstelle Leipzig, Institute for Resource Ecology, Department Reactive Transport, Permoserstraße 15, 04318 Leipzig, Germany*

[2]*Faculty for Chemistry and Food Chemistry, TU Dresden, Bergstrasse 66c, 01069 Dresden, Germany*

New 2D materials open access to a whole new world of compounds and properties. Graphene monolayer is such a material, since it has special electron transport features due to its honeycomb topology. Apart from the honeycomb net, there are many more topologies, which promise a manifold of new properties, e.g. the kagomé or the Lieb lattice. As recently shown in the case of the kagomé net, 2D polymers (covalent organic frameworks) can be designed in a way, that their geometric and electronic structures match the desired topology.[1] Other nets, e.g. the Lieb lattice, can at the moment only be realized as optical lattices or via adsorption of molecules on a surface.[2]

In this project, we want to work out the relation between topology and electronic properties. For this purpose, we employ a tight-binding model. In Fig. 1, exemplary results for the aforementioned kagomé and Lieb lattices are shown. Based on these findings, we want to propose new 2D polymers with the desired structures and new properties using density-functional theory.
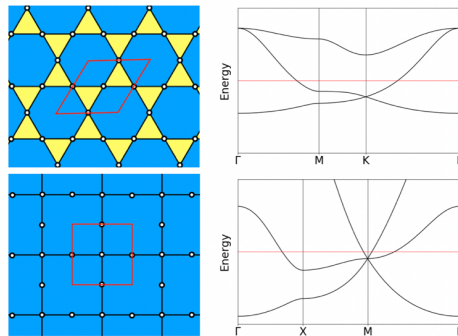

FIG. 1. Kagomé (top) and Lieb lattices (bottom) with characteristic band structures for each topology. The estimated Fermi energy is shown as a red line.

[1] Y. Jing, T. Heine, J. Am. Chem. Soc. 141, 2, 743 (2019)
[2] S. Mukherjee et al., Phys. Rev. Lett. 114, 245504 (2015); S. Taie et al., Sci. Adv. 1, e1500854 (2015); M. R. Slot et al., Nat. Phys. 13, 672 (2017)

Poster-Tu12

Phonon dispersion relation and resonances of valleydepolarization in single-layer TMDCs

Hans Tornatzky,[1] Roland Gillen,[2] Hiroshi Uchiyama,[3] and Janina Maultzsch[2]

[1]*Institute of solid state physics, Technische Universität Berlin, 10623 Berlin, Germany*

[2]*Department Physik, Friedrich-Alexander Universität Erlangen Nürnberg, 91058 Erlangen, Germany*

[3]*Super Photon Ring 8-GeV (SPring8), JASRI, Hyogo 679-5198, Japan*

We present the first experimental, full basal plane phonon dispersion, determined by inelastic X-Ray scattering with accompanying van-der-Waals corrected DFT-D3 simulations [1]. The implementation of the vdW-correction, allows the simulation of both the dispersion and structual properties, not given in commonly used LDA / PBE calculations. From our calculations, we show the displacement patterns of phonons at the K and M points, allowing further considerations regarding, e.g., scattering selection rules.

Further, we present the resonance behavior of the conservation of circular polarization in single-layer MoS_2 and $MoSe_2$ [2]. We find that the circular polarization (ρ) of the emitted light is conserved to 100% in MoS_2 and 84% / 79% (A/A$^-$ peaks) in $MoSe_2$ close to resonance. The values for $MoSe_2$ surpass any previously reported value. While our measured excitation dependent values of ρ are in good agreement with the previous reported values, the trend of ρ within the resonance of the two materials are distinctively different indicating at least two competing depolarizing processes. We will discuss popular depolarization mechanisms, taking the knowledge of the phonon dispersion into account.

[1]: H. Tornatzky, *et al.*, Phys. Rev. B (2019), in press.

[2]: H. Tornatzky, *et al.*, Phys. Rev. Lett. **121**, 167401 (2018).

Poster-Tu13

Interlayer excitons in homobilayer MoS$_2$ with strong oscillator strength

Shivangi Shree,[1] Iann C. Gerber,[1] Emmanuel Courtade,[1] Cedric Robert,[1] Takashi Taniguchi,[2] Kenji Watanabe,[2] Andrea Balocchi,[1] Pierre Renucci,[1] Delphine Lagarde,[1] Xavier Marie,[1] and Bernhard Urbaszek[1]

[1] *Universit de Toulouse INSA-CNRS-UPS, LPCNO,*
135 Avenue Rangueil, 31077 Toulouse, France

[2] *National Institute for Materials Science, Tsukuba, Ibaraki 305-0044, Japan*

The light matter interaction in semiconducting transition-metal dichalcogenides (TMDs) is governed by coulomb bound electron-hole pairs or excitons. The van der Waals TMDs heterostructures exhibit a crossover from a direct to indirect band gap material by adding one atomic layer on monolayers. The light-matter interaction is strongly modified by introducing a second layer so that new exciton complexes are formed wherein the electron and hole residing in different layers. These spatially separated particles can form a so-called interlayer exciton. Interlayer excitons in TMD heterobilayers and homobilayer show significant differences. In case of heterobilayer, interlayer excitons are indirect in both real and reciprocal space while interlayer excitons in homobilayers are indirect in real space but direct in reciprocal space.

We investigate natural AA' stacked homobilayer MoS$_2$ encapsulated in hBN and observe spin allowed interlayer excitons peak about 70 meV above the A:1s transition in reflectivity measurements (see figure 1(a) and 1(b)). The interlayer exciton oscillator strengths are around 20% of the intralayer transitions which allows us to observe the interlayer peak up to room temperature. The large oscillator strength of interlayer excitons is observed because it has partial contribution from the intralayer excitons too. This is due to delocalization of the hole state over both layers (i.e. hopping is allowed) and a well-localized electron lying in one layer as predicted by our density function theory calculations, a schematic is shown in Figure 1 (c).

In the case of a homotrilayer, the most striking result is the appearance of two peaks separated by $\sim$ 25 meV which corresponds to two different intralayer A exciton transitions. We explain the origin of splitting between the two transitions for the intralayer excitons using DFT calculations which show different energies for electron-hole pairs residing in the inner or outer layers of the homotrilayer and therefore, in agreement with the aforementioned observation. These results are reported in our recent paper [1].
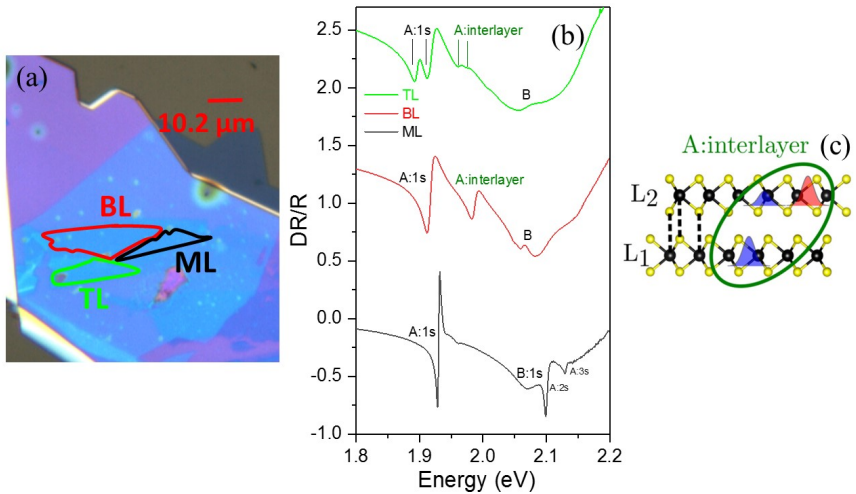

FIG. 1. *(a) Optical microscope image of the hBN/MoS$_2$/hBN heterostructure with monolayer (ML), bilayer (BL), and trilayer (TL) (b) Differential reflectivity of the three layers at temperature of T =4 K. (c) Schematics of interlayer excitons in MoS$_2$ homobilayers, an electron (red) localized on one layer interacts with a hybridized hole (blue) state to form an interlayer exciton.*

[1] Iann C. Gerber *et al.* Phy. Rev. B, **99**, 035443 (2019)

Poster-Tu14

Exciton propagation in encapsulated TMDC monolayers

Jonas Zipfel,[1] Marvin Kulig,[1] Jonas Ziegler,[1] Takashi Taniguchi,[2] Kenji Watanabe,[2] and Alexey Chernikov[1]

[1]*Department of Physics, University of Regensburg, Germany*

[2]*National Institute for Materials Science, Tsukuba, Ibaraki 305-004, Japan*

Coulomb-bound electron-hole pairs, or excitons, have been in the focus of the solid-state research for many decades[1,2]. They are of paramount importance for the fundamental understanding of interacting charge carriers in semiconductors[3,4]. More recently, they were found to dominate the electro-optical properties in single layers of semiconducting transition-metal dichalcogenides (TMDCs) and their heterostructures[5–9].

In contrast to a number of nanoscale systems, an intrinsic property of excitons in such systems, is their ability to freely move in the 2D dimensions across comparatively large distances[10], in close analogy to quantum well systems[11]. Importantly, high exciton binding energies further allow for the investigation of exciton propagation and density driven, non-linear phenomena in a broad range of experimental scenarios, including room temperature and ambient conditions. This strongly motivates detailed studies of exciton transport in two-dimensional semiconductors.

In our previous work[12], we addressed this topic by directly monitoring the spatial behavior of excitons in freestanding and supported single layers of TMDCs through spatially- and time-resolved photoluminescence microscopy. Considering the strong influence of dielectric disorder on exciton propagation we now compare these results with our recent studies of TMDC monolayers encapsulated in thin layers of high-quality boron nitride, where disorder effects can be strongly suppressed. In such systems, we find a strong increase of the effective diffusion coefficient at low exciton densities, reaching values as high as 12 cm^2/s, approximately one order of magnitude higher than in non encapsulated samples. Furthermore we find additional strong nonlinearities in the diffusion with increasing injection densities, providing more detailed insight in the physics of exciton propagation and scattering, previously obscured by disorder (figure 1).
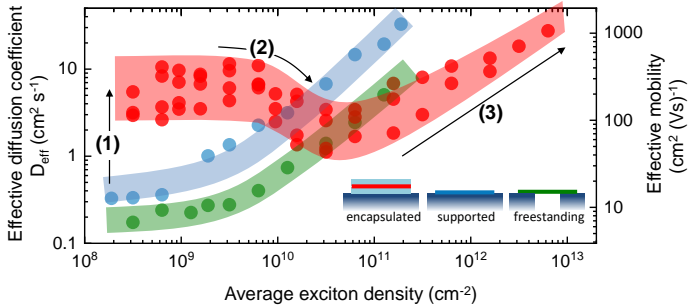

FIG. 1. *Measured effective diffusion coefficient for supported and freestanding samples (blue and green respectively)[12], as well as for a multitude of encapsulated samples (red). The three main effects in the exciton propagation in encapsulated samples are indicated by arrows.*

[1] J.Frenkel, Phys. Rev. **37**, 30 (1931).
[2] E.F. Gross and N.A. Karrjew, Dokl. Akad. Nauk SSSR **84**, 471 (1952).
[3] E.L. Ivchenko, *Optical Spectroscopy of Semiconductor Nanostructures* (Alpha Science, Harrow, England, 2005)
[4] C. Klingshirn, *Semiconductor Optics*, 3d ed. (Springer, Berlin, Heidelberg, New York, 2007)
[5] N.S. Rytova, Proc. MSU Phys., Astron. **3**, 30 (1967).
[6] L.V. Keldysh, JETP Lett. **29**, 658 (1979).
[7] P. Cudazzo, I.V. Tokatly and A. Rubio, Phys. Rev. B **84**, 085406 (2011).
[8] C. Zhang, H. Wang, W. Chan, C. Manolatou and F. Rana, Phys. Rev. B **89**, 205436 (2014).
[9] X. Xu, W. Yao, D. Xiao and T.F. Heinz, Nat. Phys. **10**, 343 (2014).
[10] N. Kumar, Q. Cui, F. Ceballos, D. He, Y. Wang and H. Zhao, Phys. Rev. B **89**, 125427 (2014).
[11] H. Hillmer, S. Hansmann, A. Forchel, M. Morohashi, E. Lopez, H.P. Meier and K. Ploog, Phys. Rev. B **38**, 5788 (1988).
[12] M. Kulig, J. Zipfel, P. Nagler, S. Blanter, C. Schüller, T. Korn, N. Paradiso, M.M. Glazov and A. Chernikov, Phys. Rev. Lett. **120**, 207401 (2018).

Poster-Tu15

Revealing the exciton masses and dielectric properties of monolayer semiconductors using high magnetic fields

A.V. Stier[1], M. Goryca[1], J. Li[1], T. Taniguchi[2], K. Watanabe[2], N.P. Wilson[3], X.Xu[3], E. Courtade[4], S. Shree[4], C. Robert[4], B. Urbaszek[4], X. Marie[4], and S.A. Crooker[1]

[1]*National High Magnetic Field Laboratory, Los Alamos National Laboratory, Los Alamos, USA*
[2]*National Institute for Materials Science, Tsukuba, Ibraki 305-0044, Japan*
[3]*Department of Physics, University of Washington, Seattle, USA*
[4]*Université de Toulouse, INSA-CNRS-UPS, LPCNO, Toulouse, France*

In semiconductor physics, many of the important material parameters relevant for opto-electronics can be experimentally revealed via optical spectroscopy in sufficiently large magnetic fields. For the new class of monolayer transition-metal dichalcogenide semiconductors, this field scale can be substantial -- many tens of teslas or more -- due to the relatively heavy carrier masses and the very large electron-hole (exciton) binding energies.

Here we present circularly-polarized absorption spectroscopy of the monolayer semiconductors WSe_2, WS_2, $MoSe_2$ and MoS_2 in pulsed magnetic fields up to 91 T [1]. By encapsulation of exfoliated monolayers in hexagonal boron nitride, we achieve sufficiently high optical quality structures that allow the observation of not only the ground state of the neutral exciton (1s) but also a number of excited *ns*-Rydberg states (up to 5s) [1,2]. We follow the magnetic field evolution of the diamagnetic shift and valley Zeeman splitting of all states.

The zero field energies in combination with the diamagnetic shifts provide a direct determination of the effective (reduced) exciton mass as well as the dielectric properties of the monolayers. Until now, these fundamental parameters were available only from theoretical calculations. Moreover, we also measure other important material properties, including exciton binding energies, exciton radii, and free-particle bandgaps. These results provide essential and quantitative parameters for the rational design of opto-electronic van der Waals heterostructures incorporating 2D semiconductor monolayers.

Unexpectedly, the measured exciton masses are significantly heavier than theoretically predicted, especially for MoS_2 and $MoSe_2$ monolayers. These results are compared with anomalously large electron masses recently revealed by transport measurements, and electron-phonon coupling effects are discussed.
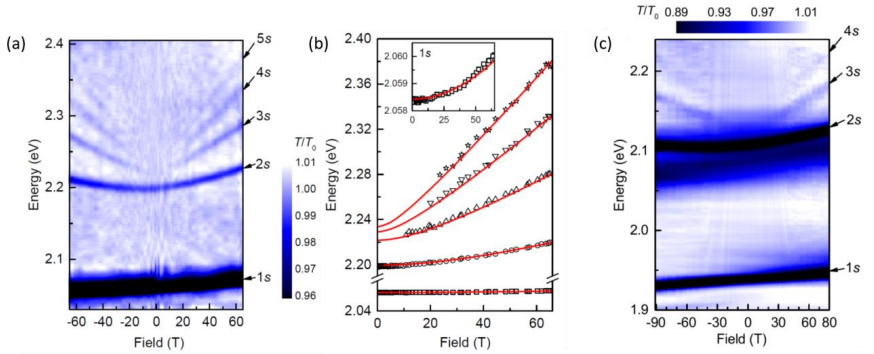

FIG. 1. (a) Intensity map of normalized transmission spectra T/T_0, from −65 to +65 T of an hBN-encapsulated monolayer of WS_2. Excellent sample quality allows observation of the 2s, 3s, 4s, and 5s excited Rydberg states of the neutral "A" exciton. (b) Average energy of the $\sigma^{\pm}$ transitions associated with transitions at the *K/K'* valleys for each *ns* Rydberg state, 1/2 $(E_{\sigma+}+E_{\sigma-})$, reveals distinct diamagnetic shifts. Solid lines show the calculated energies using the Rytova-Keldysh model. Parameters: $m_r = 0.175\ m_0$, $r_0 = 3.4$ nm, $\kappa = 4.35$, and $E_{gap} = 2.238$ eV. (c) Intensity map showing all the transmission spectra from -91 T to +80 T of an hBN-encapsulated monolayer of MoS_2. The excited 2s, 3s, and 4s Rydberg states of the neutral "A" exciton are visible. The broad feature energetically below the A:2s state is the 1s transition of the "B" exciton.

[1] M. Goryca, J. Li, A.V. Stier, S.A. Crooker, T. Taniguchi, K. Watanabe, E. Courtade, S. Shree, C. Robert, B. Urbaszek, X. Marie, *arXiv:1904.03238* (2019).
[2] A.V. Stier, N.P. Wilson, K.A. Velizhanin, J. Kono, X. Xu, S.A. Crooker, *Phys. Rev. Lett.* **120**, 057405 (2018).

Poster-Tu16

Microfocus laser-ARPES on encapsulated mono-, bi- and few-layer 1T'-WTe$_2$

Irène Cucchi,[1] Ignacio Gutiérrez-Lezama,[1,2] Edoardo Cappelli,[1] Siobhan Mckeown Walker,[1] Flavio Bruno,[1] Céline Barreteau,[1] Enrico Giannini,[1] Marco Gibertini,[1,3] Anna Tamai,[1] Alberto Morpurgo,[2] and Felix Baumberger[1,4]

[1]*Department of Quantum Matter Physics, University of Geneva,*
24 quai Ernest Ansermet, CH-1211 Geneva, Switzerland

[2]*Group of Applied Physics, University of Geneva,*
24 quai Ernest Ansermet, CH-1211 Geneva, Switzerland

[3]*National Centre for Computational Design and Discovery of New Materials (MARVEL),*
École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

[4]*Swiss Light Source, Paul Scherrer Institute, CH-5232 Villigen, Switzerland*

At the frontier between 2D materials and topological physics, 1T'-WTe$_2$ has become one of the most hotly debated transition metal dichalcogenides. For the monolayer (1L), transport measurements report edge conduction consistent with a quantum spin Hall (QSH) insulating state up to 100 K [1]. Moreover, low-temperature measurements showed the emergence of gate-tunable superconductivity, with critical temperatures up to $\sim$ 1K [2]. In bilayer (2L) form, WTe$_2$ is ferroelectric and retains its polarization above $\sim$ 20 K when it becomes metallic [3]. In addition, 2L-WTe$_2$ has been used to demonstrate the non-linear Hall effect under time-reversal invariant conditions [4].

To date, measurements of the low-energy electronic structure of exfoliated 1T'-WTe$_2$ have been lacking. Here, we demonstrate the first such measurements. This is achieved by encapsulating exfoliated WTe$_2$ with a monolayer of graphene to protect it from degradation. Direct electronic structure measurements are obtained with a novel laser-based microfocus angle-resolved photoemission (ARPES) instrument that combines 2 μm spatial resolution with low sample temperatures and high-energy resolution. Our results show a band inversion and gap opening in 1L-WTe$_2$, confirming the identification of the QSH state. For the first time, we also report direct ARPES measurements on 2L-WTe$_2$, revealing strong signature of the broken inversion symmetry. Besides advancing the interpretation of puzzling transport measurements on 2L-WTe$_2$, this experiment opens the way for electronic structure measurements on previously inaccessible ultrathin two-dimensional materials.
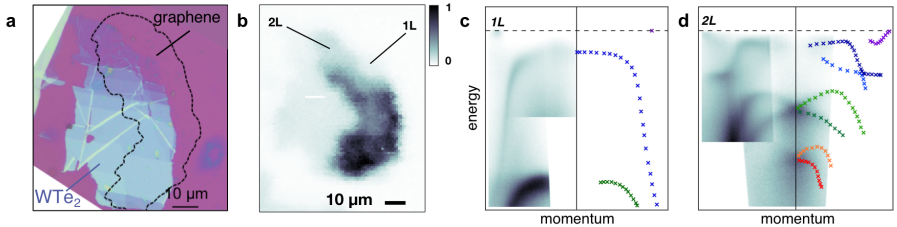

FIG. 1. *Micro-ARPES measurements on exfoliated mono- and bilayer WTe$_2$.* **a:** *Optical image of the exfoliated WTe$_2$ flake (turquoise) encapsulated in monolayer graphene (marked with a black dashed line).* **b:** *Scanned micro-ARPES image on the partially encapsulated WTe$_2$ flake, with the monolayer (1L) and bilayer (2L) regions indicated.* **c and d:** *Band dispersion of 1L-WTe$_2$ (c) and of 2L-WTe$_2$ (d) taken on the regions marked in panel b. The right hand side shows bands extracted from multiple data sets.*

[1] Wu *et al.* Science, **359**, 76, (2018)

[2] Fatemi *et al.* Science, **362**, 926, (2018)

[3] Fei *et al.* Nature, **560**, 336-339 (2018)

[4] Ma *et al.* Nature, **565**, 337-342 (2019)

Poster-Tu17

Signatures of excitons in monolayer transition metal dichalcogenides in time-resolved ARPES

<u>Dominik Christiansen</u>,[1] Malte Selig,[1] Ermin Malic,[2] Ralph Ernstorfer,[3] and Andreas Knorr[1]

[1]*Nichtlineare Optik und Quantenelektronik, Technische Universität Berlin, Berlin, Germany*

[2]*Department of Physics, Chalmers University Gothenburg, Gothenburg, Sweden*

[3]*Fritz Haber Institut Berlin der Max Planck Gesellschaft, Berlin, Germany*

Time- and angle resolved photoemission spectroscopy (trARPES), exploiting the photoelectric effect, allows to study the ultrafast dynamics of electronic excitations directly in momentum space. Typically, an optical pulse excites a non-equilibrium electron occupation, which is probed by a time-delayed ultraviolet pulse, transferring electrons from electronic semiconductor states into vacuum states. Figure 1 sketches the process of the two-photon photoemission consiting of first pumping the excitonic transition (grey dashed) and subsequently probing the valence or conduction band electrons by an XUV pulse, elevating the electrons into vacuum states. Exemplary we study atomically thin transition metal dichalcogenides (TMDCs) [1,2], which exhibit strongly bound excitons, dominating the optical properties below the free particle band gap, and a complex electronic band structure, leading to the possibility of various momentum-indirect exciton states [3], predicted to be accessible by ARPES [4,5].

Here, we develop an excitonic theory of time- and angle-resolved photoemission spectroscopy investigating the exciton dynamics in the transient regime after the optical excitation as well as the relaxation and thermalization process at longer time scales including all high symmetry points of the Brillouin zone. Shortly after excitation, we find a contribution of the coherent exciton to the trARPES spectrum and a subsequent formation of excitonic satellites due to incoherent intra- and intervalley excitons.
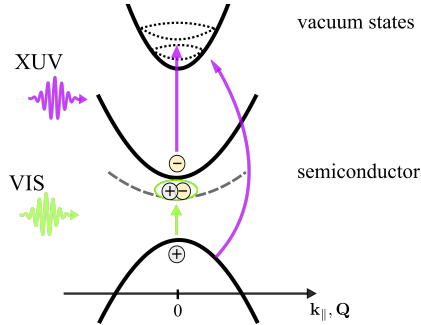

FIG. 1. *First the pump pulse excites an excitonic transition which forms via scatering events incoherent excitons (grey dashed) and second the XUV probe pulse raises an electron into the vacuum, which is then detected.*

[1] R. Bertoni et. al., Phys. Rev. Lett. **117**, 277201 (2016).

[2] M. Puppin et. al., Rev. Sci. Instru. **90**, 023104 (2019).

[3] M. Selig et. al., 2D Mater. **5**, 035017 (2018).

[4] A. Steinhoff et. al., Nat. Commun. **8**, 1166 (2017).

[5] A. Rustagi & A. F. Kemper, Phys. Rev. B **97**, 235310 (2018).

Poster-Tu18

High field magneto-transport in a hole-doped WSe$_2$ monolayer

Banan Kerdi,[1] Mathieu Pierre,[1] Michel Goiran,[1] and Walter Escoffier[1]

[1]*Laboratoire National des Champs Magnétiques Intenses (LNCMI),*
Université de Toulouse, INSA, UPS, CNRS UPR 3228, EMFL, Toulouse, France

We present magneto-transport measurements in a WSe$_2$ monolayer under pulsed magnetic field up to 58 T. A WSe$_2$ monolayer flake was deposited on an h-BN flake and contacted with platinum electrodes but without top-BN encapsulation. The sample behaves as a hole field-effect transistor when back-gated with a negative voltage, which allows the study of the valence band electronic properties with a hole concentration tuned between $7.5 \times 10^{12}\,\mathrm{cm}^{-2}$ and $5.8 \times 10^{12}\,\mathrm{cm}^{-2}$. Despite the relatively low mobility of the sample ($\sim 600\,\mathrm{cm}^2\mathrm{V}^{-1}\mathrm{s}^{-1}$) due to the lack of top-BN encapsulation, we observe clear quantum oscillations of the magneto-resistance. Our analysis of the Landau level structure is consistent with previous reports [1,2,3,4] and, thanks to the high magnetic field, we extend the previous studies to higher hole concentrations. The Landau level degeneracy is 2, which is compatible with two spin-polarized valleys, and the minima of the oscillations of R_{xx} are obtained at even filling factors. We conclude from our analysis that the ratio E_z/E_n is close to an odd integer, where E_z denotes the effective Zeeman energy and E_n the cyclotron energy. Finally, we compare these results with similar measurements in few-layer samples.
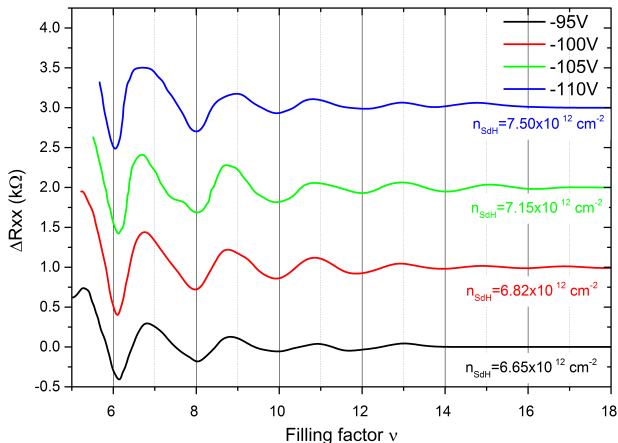
FIG. 1. *Longitudinal resistance of a WSe$_2$ monolayer, measured at 4.2 K and up to 55 T for several back-gate voltages, plotted as a function of the filling factor. A small background has been subtracted. The minima of R_{xx} are obtained at even filling factors.*

[1] B. Fallahazad *et al.*, Phys. Rev. Lett. **116**, 086601 (2016)
[2] H. C. P. Moova *et al.*, Phys. Rev. Lett. **118**, 247701 (2017)
[3] S. Xu *et al.*, Phys. Rev. Lett. **118**, 067702 (2017)
[4] M. V. Gustafsson *et al.*, Nature Materials **17**, 411 (2018)

Poster-Tu19

Time-resolved Faraday rotation on single-layer MoSe$_2$ in external magnetic fields

Simon Raiber,[1] Philipp Nagler,[1] Tobias Korn,[2] and Christian Schüller[1]

[1]*Institut für Experimentelle und Angewandte Physik,*
Universität Regensburg, 93053 Regensburg, Germany

[2]*Institut für Physik, Universität Rostock, 18059 Rostock, Germany*

We have performed time-resolved Faraday rotation (TRFR) experiments on an exfoliated MoSe$_2$ single-layer sample. After mechanical exfoliation, the sample was transferred to a c-axis-oriented sapphire substrate and mounted in a split-coil magnet cryostat, where it was held at a temperature of 1.4 K. For the TRFR experiments, two pulse trains (pump and probe pulses) with variable time delay τ, of the same mode-locked Ti:Sapphire laser with pulse lengths of about 90 fs were used. The pump pulses were circularly polarized, to resonantly excite excitons (X$_0$) or trions (negatively-charged excitons, X$^-$) selectively, either in the K$^+$ or K$^-$ valley.

Figure 1a shows three TRFR traces for three different laser energies. When the neutral exciton X$_0$ is excited resonantly (black trace in Fig. 1a), the TRFR signal has a strong fast decaying component at small τ, with a decay constant of about 180 fs, limited most likely by the ultrafast radiative recombination of the X$_0$ on a sub-picosecond timescale [1]. The strength of this ultrafast decay component is strongly reduced, when moving the laser towards lower energies (dark and light green traces in Fig. 1a). There is, however, a second, longer-lived signal component (decay constant $\sim$ 1 ps) present for all three traces, as well as a background signal, which is approximately constant within the small time window of the measurements. Such a long-lived spin polarization component was reported previously for single-layer MoSe$_2$, and attributed to a spin polarization of resident background electrons [2]. The comparatively quick loss of polarization of the free excitons X$_0$, on a picosecond timescale, is believed to be due to electron-hole exchange interaction [3,4].

In Fig. 1b we show TRFR measurements for σ^+- (solid symbols) and σ^-- (open symbols) polarized pump pulses, centered at an energy of $\sim$1660 meV, exciting selectively X$_0$ in the K$^+$ and K$^-$ valley, respectively. The black symbols represent measurements at external magnetic field $B = 0$. As expected, the signals have opposite sign [4], but are symmetric to each other, and exhibit two different decay times, each. As described above, the two times are representative of a fast radiative decay of the X$_0$, and, a slower decay of the spin polarization, which is transferred to the resident charge carriers. Interestingly, measurements at a field of $B = 4$ T in Faraday configuration (violet symbols in Fig. 1b) show: (i) an increase of the long-lived signal in σ^+ polarization (solid violet symbols in Fig. 1b), and (ii), even more interestingly, a sign change of the signal with σ^- polarized pump pulses (open violet symbols in Fig. 1b) at a time delay of about $\tau = 0.9$ ps. This may indicate an ultrafast transfer of spin/valley polarization in external magnetic fields.
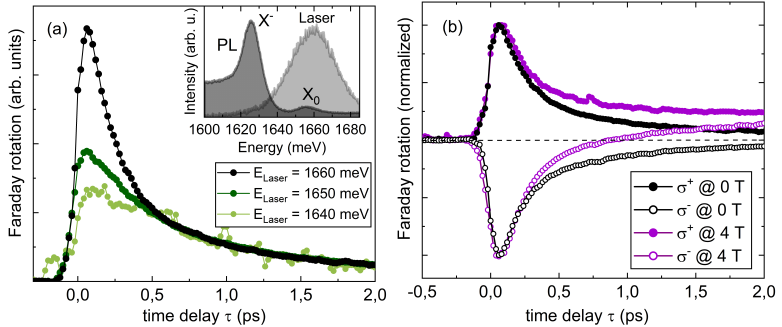

FIG. 1. (a) TRFR traces at $B = 0$ T, for different center energies (1640 meV, 1650 meV, and 1660 meV) of the pulsed laser. The inset shows a photoluminescence spectrum of the sample (dark gray), together with a laser spectrum, centered at 1660 meV (light gray). (b) TRFR traces for σ^+ and σ^- polarized pump pulses (solid and open symbols, respectively) for $B = 0$ T (black symbols) and $B = 4$ T (violet symbols). The center energy of the laser pulses is at $E = 1660$ meV, exciting the neutral exciton X$_0$ resonantly (see inset of Fig. 1a).

[1] C. Poellmann *et al.*, Nat. Materials **14**, 889 (2015), [2] M. Schwemmer *et al.*, APL **111**, 082404 (2017), [3] M. Glazov *et al.*, PRB **89**, 201302(R) (2014), [4] C. R. Zhu *et al.*, PRB **90**, 161302(R) (2014)

Poster-Tu20

High magnetic field measurements of interlayer excitons in MoSe₂-WSe₂ heterostructures

Johannes Holler,[1] Michael Kempf,[1] Jonas Zipfel,[1] Mariana V. Ballottin,[2] Anatolie A. Mitioglu,[2] Philipp Nagler,[1] Michael Högen,[1] Alexey Chernikov,[1] Peter C. M. Christianen,[2] Christian Schüller,[1] and Tobias Korn[3]

[1]*Institut für Experimentelle und Angewandte Physik, Universität Regensburg, Germany*

[2]*High Field Magnet Laboratory (HFML EMFL), Radboud University Nijmegen, Netherlands*

[3]*Institut für Physik, Universität Rostock, Germany*

In the recent years, two-dimensional materials like graphene or transition-metal dichalcogenides (TMDCs) were studied intensively. With increasing knowledge and advanced fabrication methods heterostructures became more and more interesting for research. For these two or more different van der Waals materials are stacked onto each other exhibiting new physical properties.

One of the most prominent examples for a TMDC heterostructure is MoSe₂ stacked onto WSe₂. These two materials build a staggered band alignment when stacked onto each other. Optically excited holes can then relax into the energetically favourable valence band of WSe₂ while the electrons gather in the conduction band of MoSe₂, respectively. Those spatially separated electron-hole pairs are still excitonically bound (interlayer excitons IEXs) and therefore exhibit very long photoluminescence (PL) lifetimes in contrast to intralayer excitons in the same material.

Here, we study these IEXs in MoSe₂-WSe₂ heterostructures. In low-temperature PL measurements in magnetic fields up to 30T, we observe a giant valley-selective splitting and a resulting near-unity valley polarization [1]. In time resolved measurements the expected long liftimes of the IEX can be confirmed. Also we are able to observe the build-up of the valley polarization after unpolarized excitation reavealing different dynamics and lifetimes for the different valleys.
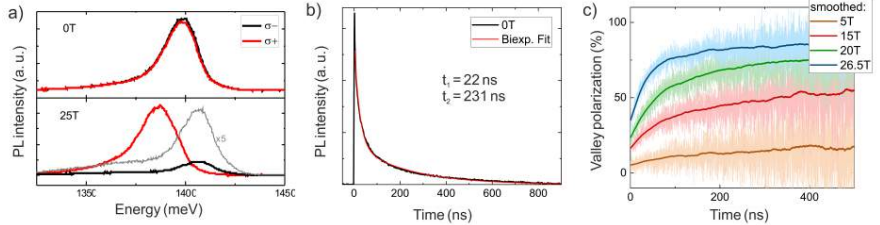

FIG. 1. *(a) Helicity-resolved PL spectra of the IEX at 0T and 25T measured using linearly polarized excitation. (b) Time-dependent measurement of the IEX PL with biexponential fit at 0T. (c) Time-dependent build-up of the valley polarization measured using linearly polarized excitation.*

[1] P. Nagler *et al.* Nat. Commun. **8**, 1551 (2017)

Poster-Tu21

Valley and Spin Dynamics in TMDCs: The Interplay of Bright and Dark Excitons

Malte Selig,[1] Florian Katsch,[1] Dominik Christiansen,[1] Ermin Malic,[2] and Andreas Knorr[1]

[1] *Nichtlineare Optik und Quantenelektronik, Technische Universität Berlin, Berlin, Germany*

[2] *Department of Physics, Chalmers University, Gothenburg, Sweden*

Atomically thin monolayers of transition metal dichalcogenides (TMDCs) exhibit strongly bound excitons which dominate the optical spectra. Besides optically bright excitons, TMDCs also possess a variety of dark exciton states: excitons with electrons and holes with opposite spin, excitons with non-vanishing angular momentum or excitons with non-vanishing center of mass momentum well above the radiative cone, including intervalley excitons. Here, we present a theory of excitonic dynamics within the Heisenberg equation of motion framework [1]: We investigate the impact of exciton phonon interaction on the excitonic lineshape [2,3,4] as well as the phonon mediated formation and relaxation dynamics of excitons [5]. It turns out, that dark states as a ground state in tungsten based TMDCs strongly influence the temporal dynamics of the exciton relaxation, as well as their luminescence yield and their resulting decay. Additionally we investigate the impact of intervalley Coulomb exchange coupling to the exciton dynamics which leads to the equilibration of selectively excited excitons at the non-equivalent corners of the Brillouin zone, cf. figure 1. In particular, we focus on the combined action of intervalley Coulomb exchange coupling and phonon mediated thermalization to intervalley exciton states giving rise to unintuitive pump probe signals, where a Pauli blocking contribution occurs at the B transition after optically exciting the energetically lower A transition. Our theoretical results are in agreement with several recent experimental observations [6,7,8].
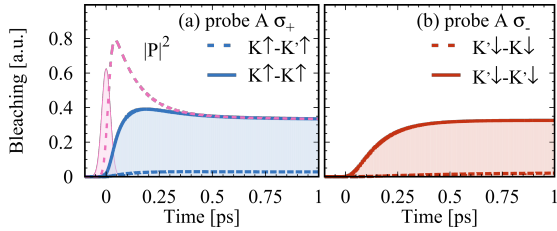

FIG. 1. *Bleaching contributions of different valley excitons to the polarization resolved pump probe signal after resonant excitation to the A exciton.*

[1] F. Katsch et al., Phys. Stat. Sol. (b) **255** 1800185 (2018).
[2] M. Selig et al., Nat Commun. **7** 13279 (2016).
[3] D. Christiansen et al., Phys. Rev. Lett. **18** 1751 (2018).
[4] I. Niehues et al., Nano Lett. **18** 187402 (2017).
[5] M. Selig et al., 2D Mater. **5** 035017 (2018).
[6] E. Pogna et al., ACS Nano **10** 1182 (2016).
[7] G. Berghäuser et al., Nat. Commun. **9** 971 (2018).
[8] Z. Wang et al., Nano Lett. **18** 6882 (2018).

Super-long-living spin excitations in a purely electronic two-dimensional gas in a strong magnetic field

S. Dickmann [1]

[1] *Institute of Solid State Physics, RAS, Chernogolovka, Moscow District, 142432, Russia*

The lowest-energy excitation in a $v = 2$ quantum Hall system is a purely electronic cyclotron spin-flip exciton (CSFE) [1] in which the electron is promoted from the upper spin sublevel (with `spin-down') of the zero Landau level to the next Landau level with `spin-up' (see Fig. 1). The CSFE energy is much smaller than the cyclotron energy: it is separated from the upper magnetoplasma mode by a negative Coulomb shift ($\Delta E_C \sim$ 1mV) and from the ground state by a gap of $\hbar\omega_c$ -ΔE_C - $\epsilon_Z \sim$ 5-7 mV. The q-momentum dispersion of

the CSFE energy is rather weak and has a smooth minimum at $q=q_0 \sim 1/l_B$ [1-2], where l_B is the magnetic length. At low temperature, T < 0.1K, the CSFE can relax only with emission of hard acoustic phonons [3]. The extremely long life of the state is determined by the following factors: (i) the relaxation studied is simultaneously an energy and a spin relaxation process, i.e. the CSFE is a `dark' exciton, the radiative relaxation suppressed; (ii) the state is energetically far from the ground state, so the emitted phonons with very short wavelengths are only weakly coupled to the state. A theoretical estimate yields the characteristic CSFE relaxation time expected to reach several milliseconds at zero

Fig. 1. Illustration of CSFE in a quantum Hall system created in a GaAs/Al-GaAs heterostructure at $v = 2$. ΔE_C is the Coulomb shift.

temperature. At higher temperatures the radiative relaxation mechanism is switched on via thermal-activation transition to the radiatively fast-relaxing upper magnetoplasma state. As a result, experimentally, even at T > 0.4K, the CSFE relaxation, actually spin relaxation, can occur with the characteristic time of 100 mcs [4-5] – which is super long for unconfined systems consisting of free conduction-band electrons. The dense CSFE ensemble (with a concentration reaching ten percent of the number of magnetic flux quanta N_ϕ) is created by resonant photoexcitation pumping. To monitor the CSFE ensemble state, an additional time-resolved technique of photoinduced resonant absorption/reflection (PIRA/R) is employed [4-5]. Experimentally, at the given CSFE concentration $n = N_x/N_\phi$ above 5 percent a threshold enhancement of the PIRA/R signal is observed when the temperature drops below some value $T_0 = T(n)$ within the 0.4K < T < 1K range [5]. This effect can be explained in the framework of the CSFE-ensemble phase transition to a coherent state, Bose-Einstein condensate. The theory describing both phases in terms of the so-called `excitonic representation' (see [2,3]) enables to estimate the correction to the CSFE energy arising from the spatial localization determined by the external smooth random potential and to explain the tenfold increase in the PIRA/R signal during the CSFE-ensemble transition to the coherent state (see `Supplementary Note 1' in Ref. [5]). Besides, this theoretical approach provides an attractive virial correction to the CSFE energy proportional to n in case the excitonic ensemble in the incoherent phase is considered as a slightly non-ideal gas [6]. Comparison of this correction to the localization energy gives an estimate of the critical concentration of the transition from the incoherent phase to the coherent one. The results are in satisfactory agreement with the experimental data.
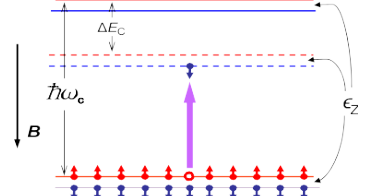
[1] C. Kallin and B.I. Halperin, *Phys. Rev. B* **30**, 5655 (1984).
[2] S. Dickmann and I.V. Kukushkin, *Phys. Rev. B* **71**, 241310(R) (2005).
[3] S. Dickmann, *Phys. Rev. Lett.* **110**, 166801 (2013).
[4] L.V. Kulik , A.V. Gorbunov, A.S. Zhuravlev, et al, *Nature Sci. Rep.* **5**, 10354 (2015).
[5] L.V. Kulik, A.S. Zhuravlev, S. Dickmann, et al, *Nature Comm.* 7, 13499 (2016).
[6] S. Dickmann, *Lithuanian Journal of Physics* (2019), in press.

Poster-Tu23

3D Printed MXene Supercapacitors

Dahnan Spurling,[1] Matthias P. Kremer,[2] John CF Zhang,[2] and Valeria Nicolosi[1]

[1] I-FORM and AMBER, CRANN, School of Chemistry, Trinity College Dublin, Dublin, Ireland

[2] AMBER, CRANN, School of Chemistry, Trinity College Dublin, Dublin, Ireland

MXenes have been well established as a suitable active material for electrodes of energy storage devices, such as supercapacitors and batteries [1]. $Ti_3C_2T_x$ is by far the most thoroughly studied member of the MXene family, and has strong pseudocapacitive behaviour arising from its surface chemistry [2]. As such, it performs exceptionally well as the active material for coplanar supercapacitors [3,4]. However, the performance of these planar devices is intrinsically limited by the fact that the third dimension is not utilised. MXene sheets in such devices tend to form a dense and homogeneous film, exhibiting high conductivity [5], but this therefore offers more restricted surface area for intercalation and pathways for ion transport [6]. By fabricating devices that make use of high surface area, three-dimensionally structured electrodes, the full capacitative performance of this material will be unlocked.

In this work, we show that Aerosol Jet printing of additive-free aqueous $Ti_3C_2T_x$ inks can be used to fabricate high aspect ratio 3D structures consisting only of MXene nanosheets. The structures can reach up to several millimetres tall with lateral resolution in the tens of micrometres. When prepared as a symmetric interdigitated supercapacitor with a gel electrolyte, the 3D structured electrodes exhibit increased capacitance, consistently larger than comparable planar devices. Figure 1 (a) shows an SEM image of a 3D printed interdigitated MXene device, (b) and (c) show cyclic voltammograms of this 3D printed device and an equivalent coplanar device respectively. The 3D printed capacitor exhibits an aerial capacitance approximately 30% higher than the coplanar device with equivalent footprint and mass loading.
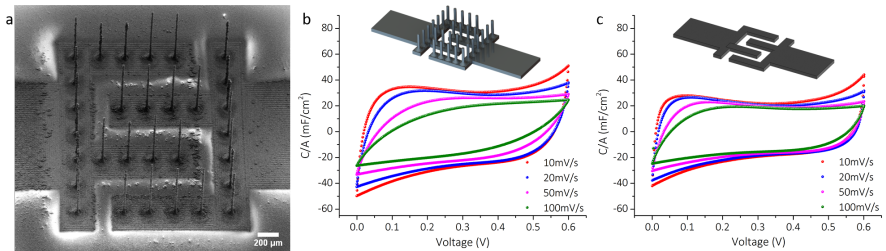

FIG. 1. (a) SEM figure of a 3D printed, interdigitated $Ti_3C_2T_x$ supercapacitor. (b) Cyclic voltammogram of the 3D device in (a). (c) a coplanar device with equivalent footprint and mass loading.

References:

[1] Anasori, B. et al. Nature Reviews Materials, **2**, 2, (2017)
[2] Hu, M. et al. ACS Nano, **10**, 12, (2016)
[3] Zhang, C. J. et al. Advanced Functional Materials, **28**, 9, (2018)
[4] Zhang, C. J. el al. Nature Communications, **10**, 1, (2019)
[5] Zhang, C. J. et al. Advanced Materials, **29**, 36, (2017)
[6] Xia, Y. et al. Nature, **557**, 7705 (2018).

Poster-Tu24

Electrical control of coherent coupling between intralayer and interlayer excitons in transition metal dichalcogenides

I. Schwartz,[1] Y. Shimazaki,[1] K. Watanabe,[2] T. Taniguchi,[2] M. Kroner,[1] and A. Imamoglu[1]

[1] Department of Physics, Institute for Quantum Electronics, ETH Zurich, Zurich 8093, Switzerland

[2] National Institute for Materials Science, Ibaraki 305-0044, Japan

Transition metal dichalcogenides (TMDs) constitute a novel platform to study exciton physics. Engineering of the exciton states in TMDs is attracting considerable attention, as evidenced by the recent reports indicating Moir excitons [1-4] and exciton state hybridization [4, 5] in TMD hetero and homo bilayers.

Here we report experimental realization of the electrical control of coherent coupling between intralayer and interlayer excitons in a tunnel coupled homo bilayer TMD. We utilized a boron nitride (BN) encapsulated $MoSe_2$ / BN / $MoSe_2$ van der Waals heterostructure, see Figure 1(a) and (b). Even though homo bilayer $MoSe_2$ has indirect gap, we observed bright intralayer exciton photoluminescence, indicating the recovery of the direct gap upon introduction of monolayer BN in between the $MoSe_2$ layers. We attribute this to the reduction of the Γ point hybridization due to the BN tunnel barrier. Interlayer excitons are evidenced in the photoluminescence spectra by the linear energy shift due to the Stark effect. Furthermore, we observed anticrossings between the intralayer and the interlayer exciton states in the gate dependence of reflectance spectroscopy, evidencing the coherent tunnel coupling of the exciton states, see Figure 1(c). The anticrossing structure appears at the crossing points of the interlayer exciton states and the bottom $MoSe_2$ intralayer exciton state under negative top gate voltage, which corresponds to the hole tunneling process. This is consistent with the low tunnel barrier of BN for the valence bands.

Our demonstration of the electrically controllable coherent coupling between intralayer and interlayer exciton states allow us to tune the permanent dipole moment and the oscillator strength of the exciton states. This adds another knob to tune the interaction between excitons, polaritons, and Fermi sea electrons, and will pave a new way to investigate many-body effect of optical excitations with electrical control in 2D materials.
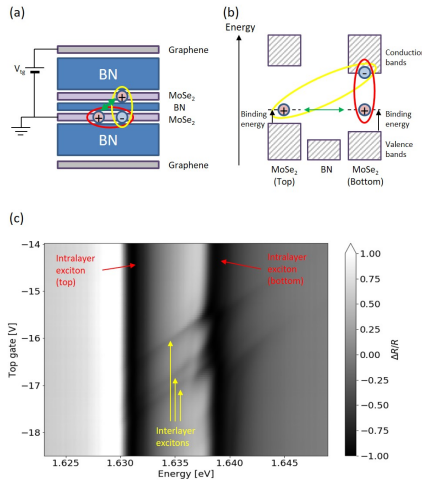

FIG. 1. (a) Schematic of the device structure. (b) Schematic of the band and exciton energy alignment. (c) Gate dependence of the reflectance spectrum, shows the Stark shift of the interlayer exciton and the anticrossing between the intralayer and interlayer excitons.

[1] K. L. Seyler et al. Nature 567, 66 (2019)
[2] K. Tran et al. Nature 567, 71 (2019)
[3] C. Jin et al. Nature 567, 76 (2019)
[4] E. M. Alexeev et al. Nature 567, 81 (2019)
[5] I. C. Gerber et al. Phys. Rev. B 99, 035443 (2019)

Poster-Tu25

CrPS$_4$ - Chromium thiophosphate - synthesis, investigation, exfoliation and all-printed detector

Adam K. Budniak,[1] Niall A. Killilea,[2] Amir Abbas Yousefi Amin,[2] Szymon J. Zelewski,[3] Jan Kopaczek,[3] Esty Ritov,[1] Yaron Kauffmann,[4] Yaron Amouyal,[4] Robert Kudrawiec,[3] Wolfgang Heiss[2] and Efrat Lifshitz[1]

[1] *Schulich Faculty of Chemistry, Technion - Israel Institute of Technology, Haifa, Israel*

[2] *Institute Materials for Electronics and Energy Technology, Friedrich-Alexander University Erlangen-Nürnberg, Erlangen, Germany*

[3] *Department of Experimental Physics, Wroclaw University of Science and Technology, Wroclaw, Poland*

[4] *Department of Materials Science and Engineering, Technion - Israel Institute of Technology, Haifa, Israel*

As graphene applications in electronics has thus far been hindered by its non-existent band gap, layered semiconductors are studied as potential candidates for future devices. One family of such are transition metal thiophosphates, denoted MPS$_x$, for x=3 or 4; for example bulk crystals of CrPS$_4$ - chromium thiophosphate – which has been examined in the past for applications in lithium batteries. Nowadays, this compound has once again gained scientific interest due to its optical anisotropic properties and the possibility to obtain and study its few- and monolayer systems [1].

In this work, bulk crystals of CrPS$_4$ were obtained by vapor transport synthesis (furnace method), followed by structure and composition confirmation via different techniques, for example Scanning Electron Microscopy with Energy-Dispersive X-ray Spectroscopy (SEM/EDX), Powder X-Ray Diffraction (PXRD). Optical properties, such as band gap and optical transitions were investigated by Solid State UV-VIS Spectroscopy, PhotoAcoustic Spectroscopy (PAS) [2] and Modulated Spectroscopy (MS) [2]. Mechanically exfoliated (Scotch-Tape method) crystals were investigated by Hi-Resolution Scanning Electron Microscope (HR-STEM) with EDX mapping revealing atom arrangement with atomic resolution EDS maps. Later, bulk crystals of chromium thiophosphate (CrPS$_4$) were exfoliated in liquid to obtain few layers systems and photoconductivity measurements were used to ascertain photoactive properties, both of re-stacked films and bulk crystals. Finally, ink from CrPS$_4$ was used to create all-printed detector, that was active in red part of visible light [3].

References:
[1] Lee et.al., ACS Nano, vol. 11, no. 11 (2017)
[2] Zelewski & Kudrawiec, Scientific Reports, vol. 7 no. 15365 (2017)
[3] Budniak et.al. in preparation

Poster-Tu26

Finite-momentum exciton landscape in mono-, bi-, and heterobilayer transition metal dichalcogenides

Thorsten Deilmann[1]

[1]*Institute of Solid State Theory, Wilhelm-Klemm-Straße 10, University of Münster, 48149 Münster, Germany*

Monolayers and bilayers of transition metal dichalcogenides are intensively studied, in particular due to their rich opto-electronic properties. Until now the main focus has been the investigation of (bright) excitons with zero momentum.

In this study we employ *ab initio* many-body perturbation theory within the GW/BSE approximation [1] to describe the entire Q-resolved exciton band structure for monolayers of the MX_2 (M = Mo, W and X = Se, S) TMDCs [2]. We find that excitonic effects strongly influence the exciton band structure, i.e. strong electron-hole interactions are present throughout the entire Q-space. While the exciton binding energies of the lowest excitons do not vary significantly with Q, we find a strong variation in their coupling strength. In particular, the latter are strongly peaked for excitons at $Q = 0$ and $Q = \Lambda$. For MoX_2 monolayers the K→K′ excitons constitute the exciton ground state (Fig. 1), while in WX_2 monolayers direct transitions at K are lowest in energy.

Our calculations further show that the exciton landscape is highly sensitive to strain and interlayer hybridization. For all four bilayers the exciton ground state is shifted to $\Gamma \rightarrow \Lambda$ or K→ Λ transitions closely following the trends of the single-particle band structures.

Finally, we extend our Q-dependent investigations to heterobilayers of MoS_2/WS_2 [2]. Such heterostructures have further promising excitations, in particular interlayer excitons and trions.
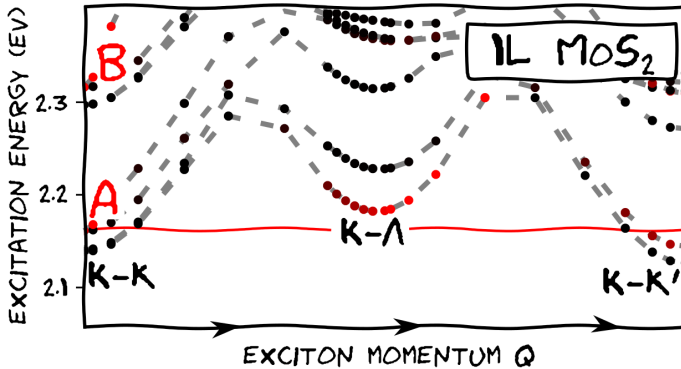

FIG. 1. *Exciton band structure of monolayer MoS_2. The grey dashed lines are a guide to the eye for the dots which denote the calculated peaks. The color corresponds to the expectation value of the dipole operator ranging from red (high amplitude) to black (zero amplitude). The horizontal red line shows the energy of the lowest bright A exciton ($Q = 0$).*

[1] Drüppel *et al.*, Phys. Rev. **B 98**, 155433 (2018)
[2] Deilmann and Thygesen, 2D Materials **6**, 035003 (2019)
[3] Deilmann and Thygesen, Nano Letters **18**, 1460–14652 (2018)

Reinforcement of poly(methyl methacrylate) by WS$_2$ nanotubes towards antiballistic applications

Saptarshi Ghosh[1], Gilad Otorgust[2], Omri Regev[3], Dan Y. Lewitus[2], Alla Zak[1*]

[1] Faculty of Sciences, Holon Institute of Technology, PO Box 305, IL-5810201 Holon, Israel

[2] Plastics and Polymer Engineering Department, Shenkar College, Ramat-Gan, 6262528 Israel

[3] Smart Technology Department, RAFAEL – Advanced Defense Systems LTD, Israel

This report investigates the credibility of inorganic nanotubes (INT) nanoparticles of tungsten disulfide (WS$_2$) to act as effective reinforcing and antiballistic agent in a poly(methyl methacrylate) (PMMA) matrixes. The inorganic nanotubes of WS$_2$ were produced via solid-gas reaction of tungsten oxides with a mixture of H$_2$/H$_2$S gases [1]. The grade of PMMA, either Acrypet VH001 or Acrypet TF8, was aptly chosen based on its suitability to the specific test - tensile and bending, or ballistic, respectively. Augmentation of mechanical features for the native polymer through addition of WS$_2$ nanostructures were initially characterized through the dynamic mechanical analysis (DMA) and tensile tests. These measurements provided a preemptive indication on the nanofillers effectiveness at different concentrations, dispersion methods, extrusion parameters, and as well as with or without compatibilizers. Under optimized conditions, the composites with INT-WS$_2$ returned notable results with an increase of ~23% in the storage modulus, improvement of ~33% for the elongation at break, of ~39% in the bending strength and of 45% for energy at break. These results are at par or even superior to existing fillers for PMMA [2]. Finally, the article reports on Split-Hopkinson Pressure Bar (SHPB) measurements where a bullet with velocity of 20 m/s was fired from gas cannon to nanocomposite plates. An obvious increase in the dynamic strength (up to 48%) for the nanocomposites compared to native polymer, as observed from the SHPB tests, projects it as a suitable candidate for future antiballistic applications. The results obtained in this work show the improvement in the elastic domain without compromising the impact resistance.
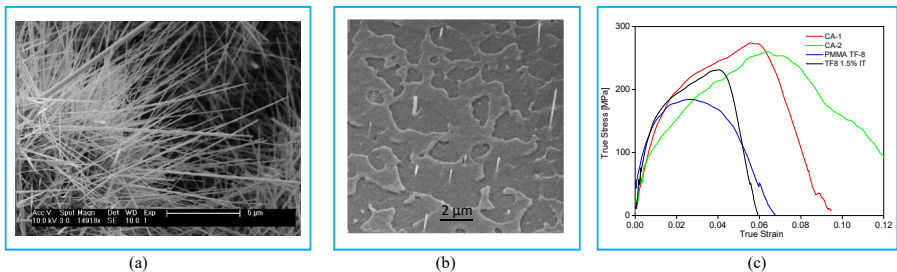

(a)   (b)   (c)

FIG. 1. (a) Scanning electron microscopic image of hedgehog structures of needle shaped INT-WS$_2$ nanofillers; (b) SEM image showing high dispersion of WS$_2$ nanotubes in PMMA, lack of agglomeration and quality adhesion through rooted tubes in polymer; (c) Dynamic strength behavior of INT-WS$_2$ – PMMA composites against native polymer (PMMA TF-8) via Split Hopkinson Pressure Bar tests. Legend: TF-8 1.5% IT - nanocomposite prepared with optimal filler concentration without compatibilizers, CA-1 and CA-2 - composites with 1.5 wt% and 3 wt% compatibilizers, respectively, along with optimal filler concentrations.

[1] A. Zak, L. Sallacan-Ecker, A. Margolin, M. Genut, R. Tenne, Nano, 4, 91, (2009)

[2] M. Ozkutlu, C. Dilek, G. Bayram, Compos. Struct. 202, 545, (2018)

Poster-Tu28

Environmental degradation of 2D GaSe photodetectors

Qinghua Zhao,[1] Riccardo Frisenda,[1] and Andres Castellanos-Gomez[1]

[1] *Instituto de Ciencia de Materiales de Madrid (ICMM-CSIC),E-28049, Madrid, Spain*

Gallium selenide (GaSe) is a novel two-dimensional material, which belongs to the layered III-VIA semiconductors family and attracted interest recently as it displays single-photon emitters at room temperature and strong optical non-linearity.[1,2,3] Nonetheless, few-layer GaSe is not stable under ambient conditions and it tends to degrade over time. Here I will discuss optoelectronic measurements of thin GaSe photodetectors to study the long-term stability.[4] We found that the GaSe flakes exposed to air tend to decompose forming firstly amorphous selenium and Ga_2Se_3 and subsequently Ga_2O_3. While the first stage is accompanied by an increase in photocurrent, in the second stage we observe a decrease in photocurrent, which leads to the final failure of GaSe photodetectors. Additionally, we found that the encapsulation of the GaSe photodetectors with hexagonal boron nitride (h-BN) can protect the GaSe from degradation and can help to achieve long-term stability of the devices.
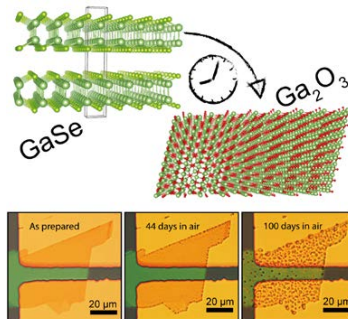

FIG. 1. The Schematic of environmental degradation process and the surface morphology evolution of 2D GaSe photodetector in the air.

[1] P. Tonndorf, S. Schwarz, *et al.*, 2D Materials, 4 (2017) 021010
[2] X. Zhou, J. Cheng, *et al.*, Journal of the American Chemical Society, 137 (2015) 7994
[3] W. Jie, X. Chen, *et al.*, Angewandte Chemie International Edition, 54 (2015) 1185
[4] Zhao Q, Frisenda R, *et al.*, Advanced Functional Materials, 28(47) (2018) 1805304

Poster-Tu29

Mechanical exfoliation and characterization of silicon phosphide

Félix Carrascoso-Plana,[1] Gabriel Sánchez-Santolino,[1] Jürgen Bauer,[2] Mar García-Hernández,[1] Riccardo Frisenda,[1] and Andrés Castellanos-Gómez[1]

[1]*Material Science Factory, Instituto de Ciencia de Materiales de Madrid (ICMM-CSIC), Madrid, Spain*
[2]*Smart-Elements GmbH*

Every time a new two-dimensional material is isolated, interesting results are obtained. These materials have gained popularity since graphene was discovered in 2004; however, the lack of a bandgap is the main weakness of graphene, which limits its applications in thin film transistors and digital integrated circuits [1]. This is why the research about two-dimensional materials is becoming more and more important nowadays.

Silicon phosphide (SiP) is a layered semiconductor with indirect bandgap (1.7eV) in its bulk form which exhibits a transition to bigger direct bandgap (2.6eV) when it is reduced to a monolayer [2]. Nevertheless, despite existing theoretical studies about this material [2], [3], it has never been experimentally explored.

In this work, we present a summary of different results that were obtained after exfoliating (mechanically) SiP crystals. This is the first time that a material which belongs to the silicon monopnictides family is exfoliated, obtaining thin flakes that were characterized in detail and were employed in order to assemble devices to perform electronic and optoelectronic measurements.
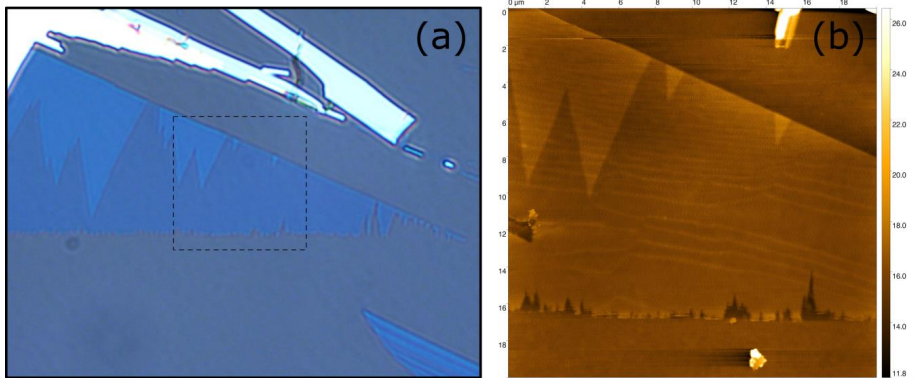

FIG. 1. (a) Optical picture of a SiP flake on Si/SiO₂. (b) AFM figure of the same device.

[1]   F. Schwierz, *Nat. Nanotechnol.*, vol. 5, no. 7, pp. 487–496, Jul. 2010.
[2]   S. Zhang *et al.*, *2D Mater.*, vol. 4, no. 1, p. 015030, Dec. 2016.
[3]   Z. Ma, J. Zhuang, X. Zhang, and Z. Zhou, *Front. Phys.*, vol. 13, no. 3, p. 138104, Mar. 2018.

Poster-Tu30

Magneto-optical investigation of valley coherence in monolayer dichalcogenides

A. A. Mitioglu,[1,2] M. V. Ballottin,[1] S. Anghel,[2] L. Kulyuk,[2] and P. C. M. Christianen[1]

[1]*High Field Magnet Laboratory (HFML-EMFL),*
Radboud University, NL-6525 ED Nijmegen, The Netherlands

[2]*Institute of Applied Physics, Academiei Street 5, MD-2028 Chisinau, Republic of Moldova*

Monolayer transition metal dichalcogenides (TMDs), such as MoS_2, $MoSe_2$, WS_2 and WSe_2, are novel two dimensional materials with a direct bandgap located at two degenerate valleys (K^+ and K^-) at the corners of the hexagonal Brillouin zone. The energy bandgap lies in the visible spectral range, which gives rise to efficient light emission and absorption. The optical spectra in monolayer TMDs are dominated by excitonic effects due to strong 2D confinement and electron-hole exchange[1]. Strong spin-orbit interaction and optical selection rules enable the creation of excitons in a specific valley using circularly polarized light. In addition, linearly polarized illumination leads to excitons, whose states are a superposition of those of K^+ and K^- valleys, which also emit linearly polarized light due to *valley coherence.*

The micro-photoluminescence (PL) spectra of TMDs are dominated by sharp neutral and charged exciton (trion) lines. Recently, we reported the control of the neutral exciton valley coherence in monolayer WS_2 with an out-of-plane magnetic field (B) up to 25 T[2]. The B induced valley Zeeman splitting causes a rotation of the exciton linear polarization with respect to the excitation. The effect was found to be due to the rotating polarization in the far-field superposition of the PL. As a result, we extracted a valley decoherence time constant of T_{s2}^*=260 fs. Similar effects have been also reported by other groups with a different interpretation, however, in terms of a Hanle effect and attributed to dephasing processes[3,4]. While the control of exciton valley coherence has now been demonstrated, fundamental questions remain about the valley decoherence mechanism.

Our recent linearly polarized-resolved PL experiments on WSe_2 monolayers reveal that up to 25 T the neutral exciton linear polarization rotates with respect to the excitation by up to 40° with a reduction of the degree of linear polarization by up to 15%. Thus WSe_2 and WS_2 behave similarly although the precise polarization rotation and depolarization parameters are slightly different. These parameters are the key towards the understanding of the exciton valley coherence. In order to better understand the valley decoherence mechanism, we performed linear polarization resolved PL measurements in uniaxially strained WSe_2 monolayer flakes. We find that the low (X_X) and high (X_Y) energy exciton branches exhibit distinct behaviour of the degree of linear polarization and rotational angle (Fig.1). These measurements allow us to extract the valley coherence time constants for both exciton components. For the high energy transition of the exciton, the valley coherence time $\simeq$ 0.45 ps, closely matches T_{s2}^* of an unstrained monolayer ($\simeq 0.34$ ps)[4]. For the low energy

FIG. 1. (a) Rotation angle and (b) degree of linear polarization for strained (X_X, X_Y) neutral excitons in WSe_2 monolayer at different B (symbols). The solid lines are fits to the data by $\theta_{X(Y)} = \arctan(\Omega_{X(Y)} T_{s2}^*)/2$.

exciton, however, T_{s2}^* is four times larger $\simeq 1.97$ ps. We attribute this effect to complex relaxation channels in-between the bright exciton active levels[5] and the longer exciton lifetime for the higher energy state than the low energy state[6]. Our results elucidate the exciton valley decoherence mechanism, which will lead to a better understanding and control of the exciton valley coherence in 2D dichalcogenides[6].
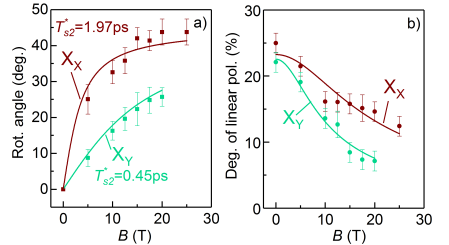
[1] X. Xu, et al., Nat. Phys. **10**, 343 (2014).
[2] R. Schmidt et al., Phys. Rev. Lett. **117**, 077402 (2016).
[3] G. Aivazian et al., Nature Physics **11**, 148 (2015).
[4] G. Wang et al., Phys. Rev. Lett. **117**, 187401 (2016).
[5] A. Mitioglu et al., Phys. Rev. B. **98**, 235429 (2018).
[6] A. Mitioglu et al., Phys. Rev. B. **99**, 155414 (2019).

The effect of h–BN encapsulation on vibrational modes in few–layer MoTe$_2$

M. Grzeszczyk[1], M. R. Molas[1], M. Bartoš[2], K. Nogajewski[1], T. Taniguchi[3], K. Watanabe[3], M. Potemski[1,2], A. Babiński[1]

[1]*Faculty of Physics, University of Warsaw, Warsaw, Poland*
[2]*Laboratoire National des Champs Magnétiques Intenses, Grenoble, France*
[3]*National Institute for Materials Science, Tsukuba, Ibaraki, Japan*

Transition metal dichalcogenide (TMD) layers and structures have emerged as an intensively investigated group of novel 2D systems, which show great potential for a wide range of electronic and optical applications. It has recently been shown that crucial for the full exploitation of their unique features is the high quality of their surfaces and interfaces. The encapsulation of TMD monolayers in hexagonal BN (h–BN) leads to substantial improvement of their optical properties, which results in narrowing of excitonic resonances observed in photoluminescence experiment [1].

In this communication we show that the h–BN encapsulation results in modification of the vibrational spectra of few–layer TMDs. We present the results of Raman scattering (RS) measurements (1.96 eV excitation at room temperature) on pristine (placed on SiO$_2$/Si substrate) and h–BN encapsulated few-layer MoTe$_2$ layers. A substantial blueshift and redshift of the correspoding out-of-plane (A_1'/A_{1g}) and in-plane (E'/E_{2g}^1) modes in the encapsulated layers have been observed, as illustrated in the Figure 1. On the other hand, the encapsulation does not significantly affect the spectral widths of the phonon lines. Unchanged is also the fine structure of the out-of-plane modes due to Davydov splitting. We discuss our results in terms of a force constant model [2]. We show that the additional van der Waals (vdW) interactions with the encapsulating layer modify the interatomic forces in few layer MoTe$_2$.

Figure 1: (a) RS spectra of h–BN encapsulated and pristine MoTe$_2$ flakes. (b) Peak frequency versus thickness of MoTe$_2$ flakes.

We believe that our study can lead to better understanding of crystal lattice dynamics of vertically stacked vdW layers and will trigger more theoretical and experimental work extending over other TMD systems.
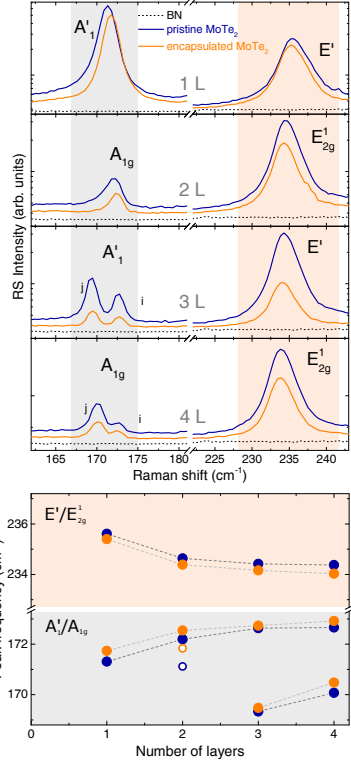
[1] O. Ajayi et al. *2D Materials* **4**, 031011 (2017)
[2] G. Froehlicher et al., *Nano Letters* **15**, 6481-6489 (2015)

Interlayer interaction and band mixing in van der Waals semiconductors under high magnetic fields

A. Arora[1,2], M. Koperski[1,3,4], A. Slobodeniuk[1], T. Deilmann[5], K. Nogajewski[1,6], R. Schmidt[2], R. Schneider[2], M. R. Molas[1,6], S. Michaelis de Vasconcellos[2], M. Rohlfing[5], R. Bratschitsch[2], and M. Potemski[1]

[1]Laboratoire National des Champs Magnétiques Intenses, CNRS-UGA-UPS-INSA-EMFL, 25 rue des Martyrs, 38042 Grenoble, France

[2]Institute of Physics and Center for Nanotechnology, University of Münster, Wilhelm-Klemm-Strasse 10, 48149 Münster, Germany

[3]School of Physics and Astronomy, University of Manchester, Oxford Road, Manchester, M13 9PL, United Kingdom

[4]National Graphene Institute, University of Manchester, Oxford Road, Manchester, M13 9PL, United Kingdom

[5] Institute of Solid State Theory, Wilhelm-Klemm-Straße 10, University of Münster, 48149 Münster, Germany

[6] Institute of Experimental Physics, Faculty of Physics, University of Warsaw, Pasteura, 5, 02-093, Warszawa, Poland

Hybridization of electronic states in van der Waals-coupled layers of semiconducting transition metal dichalcogenides (TMDCs) significantly affects their energy bands and electronic properties. In TMDC multilayers, a strong spin-layer locking leads to the creation of intralayer and interlayer excitons upon optical excitation. Band mixing induced by the interlayer interaction affects the magnetic moments associated with the conduction and valence band states and can be accessed through Zeeman spectroscopy of these exciton states [1].

We perform helicity-resolved magneto-reflectance spectroscopy of excitons in WSe_2, $MoSe_2$ and $MoTe_2$ crystals of thickness from monolayer to the bulk limit under high magnetic fields of up to 30 T. The ground state A excitons exhibit a monolayer-like valley Zeeman splitting with a negative g-factor, whose magnitude increases monotonically when the crystal thickness decreases from bulk to a monolayer. However, interlayer excitations have a valley Zeeman splitting of opposite sign [2,3]. Using combined *GW*-BSE ab initio and **kp** calculations, we demonstrate that the observed thickness-dependent g-factors for different TMDC materials are well accounted for by the hybridization of electronic states in the K valleys. For example, mixing of the valence and conduction band states induced by the interlayer interaction decreases the g-factor of the ground-state A excitons with increasing layer number (Fig. 1). This effect is largest for $MoTe_2$, followed by $MoSe_2$, and smallest for WSe_2 [1]. In addition, we will discuss this phenomenon also for the interlayer excitons.

Our results represent the first report devoted to the effect of band hybridization on the magneto-optics of multilayer TMDCs, and contribute towards a better understanding of layered TMDCs along with future device-based applications.
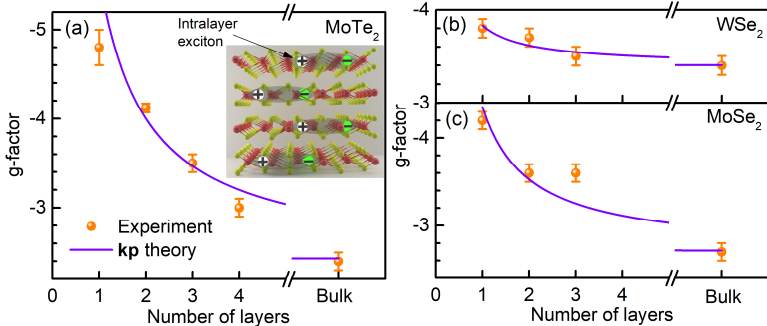

FIG. 1 Effective g-factors of ground state A exciton in (a) $MoTe_2$, (b) WSe_2, and (c) $MoSe_2$ as a function of layer thickness measured using helicity-resolved high-field magneto-reflectance spectroscopy (orange points), along with the **kp** theory fit. The inset of (a) depicts visualizes monolayer-like intralayer excitons in a multilayer TMDC, due to a strong confinement of the exciton wave function within individual layers.

[1] A. Arora et al., 2D Mater. **6**, 015010 (2018)
[2] A. Arora et al., Nanoscale **10**, 15571 (2018)
[3] A. Arora et al., Nat. Commun. **8**, 639 (2017)

Poster-Tu33

Atomic-scale control over the structure of 2D transition metal dichalcogenide alloys through atomic layer deposition

Jeff J.P.M. Schulpen,[1] Vincent Vandalon,[1] Shashank Balasubramanyam,[1]
Akhil Sharma,[1] W.M.M. (Erwin) Kessels,[1] and Ageeth A. Bol[1]

[1]*Faculty of Applied Physics, Eindhoven University of Technology, Eindhoven, The Netherlands*

Two-dimensional transition metal dichalcogenides (2D-TMDs) are highly promising materials for electronic and photonic applications. One of the prime requirements for their usability is an exact understanding and control of their electronic structure. An appealing method of achieving such control is through alloying. As an example, the TMD pair MoS_2 and WS_2 have near-perfect lattice matching but distinctly different electronic structures (bandgaps of 1.8 and 2.0 eV respectively). As such, they may be combined into $Mo_xW_{(1-x)}S_2$ alloys with minimal structural distortion and electronic properties intermediate to MoS_2 and WS_2.

In this work, we employ atomic layer deposition (ALD) for the synthesis of $Mo_xW_{(1-x)}S_2$ alloys, demonstrating fine control over the alloy ratio x as verified by x-ray photoelectron spectroscopy. We employ spectroscopic ellipsometry, photoluminescence spectroscopy and absorption spectroscopy to investigate the electronic structure of the alloys and show their continuous tunability as a function of the alloy ratio x. Comparing the experimental results to ab-initio calculations suggests that grain size is the dominant factor in determining the resistivity for ALD-synthesized alloys, whereas the band gap is mainly determined by the alloy ratio.

Beyond that, we present evidence that a supercycle approach to ALD (see figure 1) enables tunable electronic structure of $Mo_xW_{(1-x)}S_2$ alloys even at constant x through the exact ordering of the ALD cycles. Effects of this ordering on the crystal structure are demonstrated by Raman spectroscopy, where the two A_{1g} vibrational peaks merge together as the ALD cycle ordering is made to be more well-mixed (see figure 1). Ab-initio calculations suggest that this shift in vibrational frequencies is related to the atomic-scale ordering and clustering of MoS_2 and WS_2 unit cells within the alloy. This indicates that the atomic-scale growth control inherent to the atomic layer deposition technique may be used as a means of achieving very fine tunability in these alloys. Further work will focus on how the demonstrated atomic-level control in the $Mo_xW_{(1-x)}S_2$ alloys impacts their electronic structure.
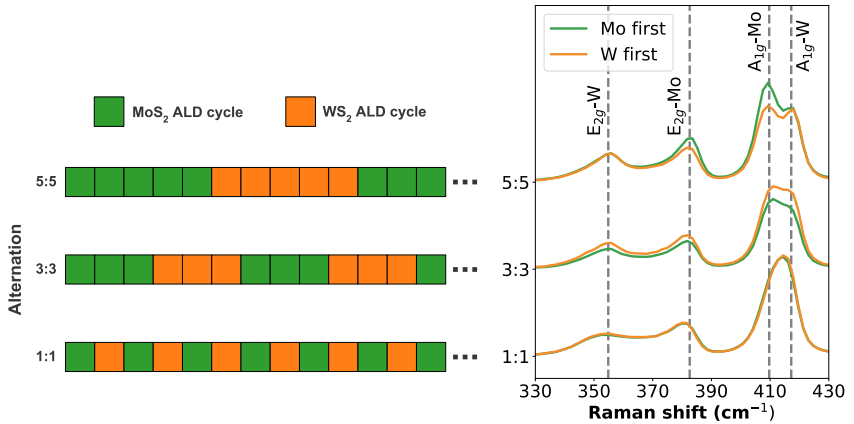

FIG. 1. *Supercycle ALD recipes (left) and Raman spectra (right) of $Mo_{0.5}W_{0.5}S_2$ alloys with three different degrees of mixing. The convergence of the A_{1g} vibrational peaks as a function of the degree of mixing is indicative of changes to the atomic-level structure of the alloys.*

Poster-Tu34

Magnetic shifts of monolayer and interlayer excitons in transition metal dichalcogenide-based systems: theory and experiment

T. Woźniak,[1, 2] S.-Y. Chen,[3, 4] A. Chaves,[5] D. Smirnov,[6] G. Seifert,[1] D. R. Reichman,[7] T. Korn,[8] J. Yan,[3] and J. Kunstmann[1]

[1] *TU Dresden, 01062 Dresden, Germany*

[2] *Wrocław University of Science and Technology, Poland*

[3] *University of Massachusetts, Amherst, USA*

[4] *ARC Centre of Excellence in Future Low-Energy Electronics Technologies, Australia*

[5] *Universidade Federal do Ceará, Fortaleza, Brazil*

[6] *National High Magnetic Field Laboratory, Tallahassee, USA*

[7] *Columbia University, New York, USA*

[8] *University of Rostock, Germany*

Optical spectra of transition metal dichalcogenides (TMD) exhibit pronounced excitonic peaks. Their energy shifts in high magnetic fields reflect multiple aspects of the system's electronic structure. The Zeeman shift, as quantified by its g-factor, is associated with the properties of the involved electron and hole states and the diamagnetic shift is related to the spatial extend of the excitonic wave function. Here we combine experiment and theory to study magnetic shifts of excitonic lines in TMD monolayers, bilayers and heterostructures.

We present a scheme that allows to calculate g-factors from band structure calculations, using either first principles methods or model Hamiltonians. Results for monolayer Rydberg excitons, interlayer excitons, and momentum indirect excitons in TMD homo- and heterostructures are discussed.

For monolayer WSe_2, encapsulated in hexagonal boron nitride, we observe radiative recombination from Rydberg excitons up to the 4s excited state in magneto-photoluminescence spectroscopy. We confirm the progressively larger exciton size for higher energy excited states through diamagnetic shift measurements. The Zeeman shift of the 1s to 3s states, from both luminescence and absorption measurements, exhibits a monotonic increase of g-factor, reflecting nontrivial magnetic-dipole-moment differences between ground and excited exciton states. This systematic evolution of magnetic dipole moments is theoretically explained from the spreading of the Rydberg states in momentum space (see Fig. 1 and [1]).
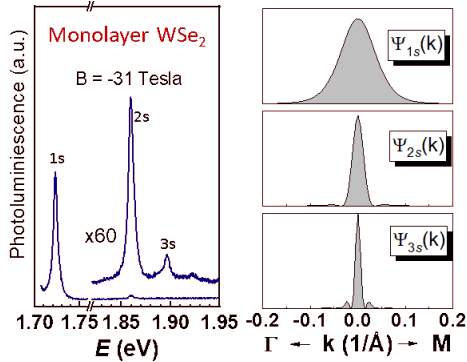

FIG. 1.   *(left) Photoluminescence spectrum of WSe_2 at a magnetic field of -31 Tesla. Emission from 1s, 2s and 3s excitons is observed. (right) The spread of the exciton wave functions in momentum space can explain the increase of the g-factor from 2.15, for the 1s exciton, to 2.53, for the 3s exciton. [1]*

[1] Chen *et al.*, Nano Lett. **19**, 2464-2471 (2019).

361 Poster-Tu35

Tuning the valley polarization in monolayer MoS$_2$ at room temperature

Bastian Miller[1], Jessica Lindlau[2], Andre Neumann[2], Alexander Holleitner[1], Alexander Högele[2] and Ursula Wurstbauer[3]

[1]*Walter Schottky Institute and Physics-Department, Technical University of Munich, Germany.*

[2]*Fakultät für Physik, Munich Quantum Center, and Center for NanoScience (CeNS), LMU Munich, Germany.*

[3]*Institute of Physics, University of Münster, Germany*

A direct band gap [1], remarkable light-matter coupling [2] as well as strong spin-orbit and Coulomb interaction establish two-dimensional (2D) crystals of transition metal dichalcogenides (TMDCs) as an emerging material class for fundamental studies as well as novel technological concepts. Valley selective optical excitation allows for optoelectronic applications based on the momentum of excitons [3]. In addition to lattice imperfections and disorder, scattering by phonons is a significant mechanism for valley depolarization and decoherence in TMDCs at elevated temperatures preventing high-temperature valley polarization required for realistic applications [4]. Thus, a detailed knowledge about strength and nature of the interaction of excitons with phonons is vital. We directly access exciton-phonon coupling in charge tunable single layer MoS$_2$ devices by polarization resolved Raman spectroscopy. We observe a strong defect mediated coupling between the long-range oscillating electric field induced by the longitudinal optical (LO) phonon in the dipolar medium and the exciton. We find that this so-called Fröhlich exciton LO-phonon interaction [5] is suppressed by doping. This suppression correlates with a distinct increase of the degree of valley polarization of up to 60% even at elevated temperatures of 220 K and still distinct at room temperature [6]. Our result demonstrates a promising strategy to increase the degree of valley polarization towards room temperature valleytronic applications.
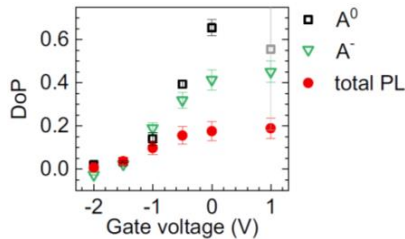
FIG. 1. Degree of polarization at T = 220K as a function of the charge carrier density of the total PL and of the individual contributions of the neutral (A0) and charged (A−) exciton obtained from peak fits. The error bars denote the standard deviation from the fit approach. The charge carrier density is depleted with increasing gate volatage. modified from [6])

[1] K. F. Mak et al., Phys. Rev. Lett. 105,136805 (2010).
[2] U. Wurstbauer et al., J. Phys. D. Appl. Phys. 50, 173001 (2017).
[3] K. F. Mak et al., Nat. Nanotechnol. 7, 494 (2012).
[4] H. Zeng et al., Nat. Nanotechnol. 7, 490 (2012).
[5] H. Fröhlich, Adv. Phys. 3, 325 (1954).
[6] B. Miller et al. Nature Commun. **10**, 807 (2019).