Thursday Posters

Poster-Th01

Pentacene meets transition metal dichalcogenides for solar energy conversion

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Combining two-dimensional (2D) materials with organic materials can be very attractive for applications that require flexibility and where size and weight are important parameters to be considered, such as in wearable, portable and mobile applications. Organic materials usually exhibit excellent optical absorption efficiency and photo- and temperature-induced conformational changes, while 2D materials often show relatively high carrier mobility, superior mechanical flexibility, and tunable electronic and optical properties. Combining both systems can stabilize the organic materials and lead to heterostructures with both high carrier mobility and high optical absorption efficiency, which is promising for solar energy conversion. In this work we investigate, by means of density-functional-theory calculations, heterostructures composed of pentacene molecules and transition metal dichalcogenides (TMD) for application in photovoltaic devices. We examine the interaction between the molecules and monolayer TMDs as well as the band alignment of the heterostructures, considering effects of the molecular coverage and dielectric screening. Our results show that the band edge positions of pentacene change significantly when going from the isolated molecule to the monolayer coverage, affecting the band alignment with a TMD monolayer.

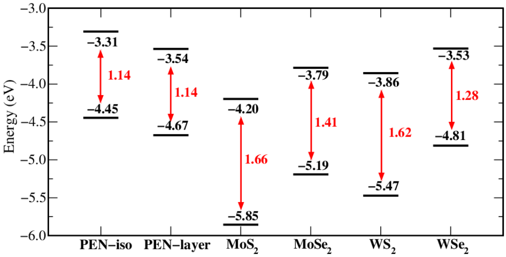

FIG. 1. *Band alignment (computed at the PBE level and including spin-orbit coupling) between pentacene molecules and monolayer TMDs. For the molecules we considered an isolated molecule (PEN-iso) as well as monolayer coverage in a (6 × 3) supercell (PEN-layer). The position of the band edges and the values of the band gaps (in red) are given in eV.*

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Comparison of density functional theory methods in layered MS_2 compounds under compression

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We report high-pressure Raman-scattering measurements on the transition-metal dichalcogenide (TMDC) compound HfS_2. The aim of this work is twofold: (i) to investigate the high-pressure behavior of the zone-center optical phonon modes of HfS_2 and experimentally determine the linear pressure coefficients and mode Grüneisen parameters of this material; (ii) to test the validity of different density functional theory (DFT) approaches in order to predict the lattice-dynamical properties of HfS_2 under pressure. For this purpose, the experimental results are compared with the results of DFT calculations performed with different functionals, with and without van der Waals (vdW) interaction corrections. We find that DFT calculations within the generalized gradient approximation (GGA) properly describe the high pressure lattice dynamics of HfS_2 when vdW interactions are taken into account. In contrast, we show that DFT within the local density approximation (LDA), which is widely used to predict structural and vibrational properties at ambient conditions in 2D compounds, fails to reproduce the behavior of HfS_2 under compression. Similar conclusions are reached in the case of MoS_2. This suggests that large errors may be introduced if the compressibility and Grüneisen parameters of bulk TMDCs are calculated with LDA. Therefore, the validity of different approaches to calculate the structural and vibrational properties of bulk and few-layered vdW materials under compression should be carefully assessed. [1]

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Poster-Th03

Interfacial assembly of liquid-exfoliated nanosheets

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Liquid phase exfoliation (LPE) has been demonstrated to be a powerful and versatile technique for scalable production of two-dimensional (2D) nanomaterials, such as graphene and molybdenum disulfide (MoS_2) which allows for their processing into a wide range of structures. By understanding the chemical physics of their dispersion and performing applications-driven solvent selection, we are able to develop a framework for interfacial assembly of nanosheets based on their surface interactions. This facilitates formation of emulsions with stabilised by pristine few-layer nanosheets which exhibit system-scale conductivity at ultra-low loading levels. By modelling the surface interactions in such systems, we are able to measure the surface energy of the nanosheets to allow design of emulsions for specific applications. Finally, by extension to nanosheets at air/water interfaces, we are able to fabricate Langmuir films of MoS_2 nanosheets with high area coverage and conductivity at low film thickness, potentially enabling applications in solution-processed thin film electronics.

Poster-Th04

Extraordinary Conductivity in Polymer Composites by In-situ Reduction of Segregated Graphene Oxide Networks

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We observe graphene oxide-polymer latex composites which exhibit extraordinary conductivity after relatively low temperature treatment. Microstructural, chemical and thermal measurements reveal that decomposition of the graphene oxide functional groups induces aromatisation of the polymer to produce segregated system-scale conductive networks. A visible colour change, from brown to black, is correlated with the onset of conductivity and is well-described by an Arrhenius model with activation energy characteristic of decomposition of the graphene oxide epoxy groups. Simultaneously we observe mechanical reinforcement of the matrix polymer due to graphene oxide addition which is unaffected by the thermo-chemical processing. These results present a route towards high-performance, low-loading, functional composites using facile processing methodologies.

Poster-Th05

Interlayer excitons in a WSe_2/$MoSe_2$ heterobilayer van der Waals heterostructure

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III-V semiconductor heterostructures are very often used for electro-optics applications as their properties can be engineered over a wide range. However, GaAs for instance does not form a native oxide. The dangling bonds at the surface pin the Fermi energy in the energy gap, resulting typically in a large electric field at the surface. This means that the active elements in an electro-optic device must be positioned relatively far from the surface. This in turn limits the feature size that can be created by an on-surface pattern: high spatial frequencies are lost at the buried active layer. A new class of semiconductor has emerged for which this problem does not arise. In a van der Waals heterostructure, a device is constructed from individual layers, for instance graphene, hexagonal-BN, $MoSe_2$, and so on. Due to their truly two-dimensional nature each constituent performs perfectly well in its monolayer form: there are no dangling bonds.

Here, semiconducting transition-metal dichalcogenide (TMD) heterobilayers consisting of $MoSe_2$ and WSe_2 are studied. These heterobilayers form a type-II band alignment which leads to an electron potential well in the $MoSe_2$ layer and a hole potential well in the WSe_2 layer. The possibility arises of forming so-called interlayer excitons (IX) with a permanent dipole-moment and enhanced radiative-lifetime with respect to excitons in single monolayers [1].

The interlayer coupling in the bilayer depends on the relative orientation of the crystal axes of the constituent monolayers [2]. If the crystal axes of each monolayer are aligned along the same direction, the coupling is maximized. The underlying 6-fold crystal symmetry of the TMD monolayers were determined with the help of a home-built angle-resolved second-harmonic generation (SHG) setup [3]. By measuring the SHG, we determine the crystal axis orientation of the $MoSe_2$ and WSe_2 monolayers and align them while fabricating the heterostructure in order to achieve a good interlayer coupling.

The advantage of this heterobilayer over individual monolayers lies in the response to a vertical electric field. In an external electric field perpendicular to the two-dimensional layers, neutral and charged excitons experience an energy shift in accordance to the quantum-confined Stark effect (QCSE) [4]. The external electric field can be applied by embedding encapsulated TMD layers in a gated van der Waals heterostructure. The quantum-confined Stark shift has been measured for an encapsulated MoS_2 monolayer [5]. Due to symmetry reasons, the excitonic dipole moment is zero, such that the QCSE scales quadratically with the electric field. Stark shifts of about half the homogeneous linewidth were achieved, which demonstrates that excitons can be polarized [5]. However, these energy shifts are quite small. Electrical control of excitons based on the QCSE requires much larger polarizabilities or a non-zero dipole moment. In type-II TMD heterobilayers, the IXs exhibit a non-zero dipole moment. These dipole moments are aligned perpendicular to the monolayer plane [6]. Here, the Stark shift is linear as the contribution of the polarizability to the shift is much smaller compared to the contribution of the dipole moment. The total energy shift is around 40 meV, which is much larger than the shift measured for monolayer MoS_2. This large tuning range of the IX emission energy should allow us to create excitonic devices just by variation of the vertical electric field.

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Vibrational properties and charge transfer in the misfit-layer compound LaS-CrS$_2$ and nanotubes thereof

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The stacking of layered van-der-Waals materials has recently drawn a lot of attention due to the unique possibilities of tuning material properties. The sample fabrication implies on the other side meticulous handling of the layers to obtain the desired heterostructure with defined stacking order.

Misfit-layer compounds of MX-TX$_2$ structure offer an inherent stacking order of a chalcogenide and a dichalcogenide that allows tuning of the material properties by changing the elements in each sublayer in the initial growth process.[1,2] Here M is an element of the lanthanides and the TX$_2$ principally covers the whole range of the transition-metal dichalcogenides (TMDCs). In addition, similar structures like CoO$_2$ have recently been reported with intercalation of Ca$_2$CoO$_3$.[3,4]

In this study we compare the Raman spectrum of LaS-CrS$_2$ with DFT calculations of the vibrational properties of the full supercell of LaS-CrS$_2$ and compare it to the isolated subsystems LaS and CrS$_2$ as a metastable single layer.[5,6] We find a strong impact of the interlayer interaction on the Raman spectrum revealing a much more complex structure as compared to the isolated sublayers. The charge transfer upon formation of the LaS-CrS$_2$ supercell and the change in lattice parameters is extracted from the DFT calculations and discussed with respect to the Raman frequencies LaS-CrS$_2$.

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Poster-Th07

Spin-Polarized Electrons in Monolayer MoS_2

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We present experimental evidence for a spin-polarized electronic ground-state in a two-dimensional semiconductor, monolayer MoS_2 [1].

In a two-dimensional electron gas (2DEG), Coulomb effects dominate over single-particle effects in the limit of low electron-density. In this regime, the average inter-electron distance is larger than the Bohr radius in the host material. In gallium arsenide and silicon 2DEGs, electrons are localized at these low electron densities such that Coulomb effects tend to be obscured. New opportunities arise in transition-metal dichalcogenides (TMDs). A TMD monolayer represents a natural realization of a 2DEG. Significantly, the extremely small TMD Bohr-radius suggests that Coulomb effects play an important role at experimentally relevant electron-densities.

We investigate the optical absorption of a monolayer MoS_2, a member of the optically active TMD-family. The band edges are located at the K and K' points of the Brillouin zone. At realistic electron densities, there are four relevant conduction bands [2,3]: two at the K point and two at the K' point. The two bands at K, equivalently the two bands at K', carry opposite spin and are split by the spin-orbit interaction. MoS_2 is special among the TMDs in that the conduction-band spin-orbit splitting is small compared to the typical Fermi levels achieved by gating. In a single-particle picture, the electronic ground-state is formed by a near-equal filling of the four available conduction bands. We present an experiment that overturns this single-particle picture [1]. In a magnetic field applied perpendicular to the 2DEG, we find that the electrons have the same spin. Two of the four bands are occupied - the two with the same spin but at different valleys. This is a striking result: the creation of a spontaneous spin-polarization in a 2DEG.

We probe the electronic ground-state at various electron densities using optical absorption, a local, non-invasive, spin- and valley-resolved tool. At the smallest electron densities, our gated device gives a close-to-ideal exciton linewidth. On increasing the electron concentration, we observe a strong exciton-Fermi sea interaction. Specifically, we observe two low-energy trion-resonances for photons with one polarization, yet only very weak features in the other polarization. We interpret the spectra with the well-established exciton-polaron picture of optical absorption in a 2DEG [4-6]. We are led to the conclusion that the electrons are spin-polarized.

We propose that inter-valley electron-electron exchange is responsible for the spontaneous creation of a spin-polarized ground-state in electron-doped monolayer MoS_2. Even though the K and K' points are far apart in phase-space, the Bohr radius is so small that inter-valley Coulomb scattering is significant [7,8]. The Mermin-Wagner theorem prohibits a spin polarization for isotropic spins. This suggests that the small spin-orbit interaction is crucial to the explanation.

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Interlayer Coupling Implications on Optical Properties of Atomically Thin Semiconducting Materials

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Monolayer transition metal dichalchogenides (TMDs) are direct band gap semiconductors with exceptionally strong Coulomb interaction leading to the formation of tightly bound excitons. Furthermore, due to spin–orbit coupling (SOC) and broken inversion symmetry, both the absorption and the emission in monolayer TMDs show valley and spin-dependent selection rule, providing an unprecedented platform to explore valleytronics. These exotic properties make them promising materials in electronics, optoelectronics, and valleytronic applications [1].

In bilayer TMDs with inversion symmetry, the valley-dependent selection rule does not apply anymore and low valley contrast was observed in MoS2 bilayers [2] which greatly restricts the range of thickness selection for achieving potential MoS2-based valleytronic devices. In contrast to MoS2 with comparable spin-valley coupling and interlayer hopping energy, the significantly higher spin-valley coupling strength in bilayer tungsten based TMDs (WX2) leads to suppressed interlayer hopping. Therefore, WX2 bilayers possess an extra index called layer polarization in addition to valley and spin indices, paving a way to manipulation of the electronic degrees of freedom in WX2. [3] Despite the widely accepted impression that valley-induced circular polarization should be inherently absent in centrosymmetric materials, highly selective circular polarization has been reported for the direct transition in centrosymmetric bilayer WS2 and WSe2 [4] indicating that bilayer WX2 is a fascinating platform for further exploration of valley physics.

It has been shown that interlayer coupling significantly tune the optical properties of bilayer WX2. [5] So far, the experimental studies of valley properties have been performed both on mechanically exfoliated bilayer WS2 samples with quite strong interlayer coupling [4,6] and chemical vapour deposition (CVD) samples on various substrates [7]. Correlation between the intensity of the indirect bandgap emission and valley polarization has been shown, demonstrating that acoustic phonons play a leading role in the valley polarization of bilayer WS2 and the depletion of such phonons in the indirect optical transition process contributes to the exceptionally robust valley polarization.

In this work we investigate WX2 bilayers in order to understand influence of various factors on interlayer coupling strength and its implication on optical properties of atomically thin semiconductors.

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Poster-Th09

Surfactant free, Liquid Exfoliated Copper Hydroxide Non-Enzymatic Glucose Detector

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Layered Double Hydroxides (LDHs) have attracted a wide range of interest in the field of electrochemistry including energy storage, energy conversion and sensing applications. In this talk, a copper hydroxide LDH based glucose sensor will be presented.

Isolation of LDHs are often produced by direct synthesis or ion intercalation of bulk-hydrogen bonded compounds. Recently, liquid exfoliation of a wide range of these materials in surfactant and solvent has been demonstrated[1]. Avoiding surfactant is a desirable avenue to prevent degradation of the electrochemical properties of the thin films and low-boiling point solvents present their own challenges. To resolve these issues a range of solvents including alcohol-water blends are used to produce stable dispersions of copper hydroxide.

The stabilised dispersion can be further size selected using cascade centrifugation. These samples show increasing electrochemical sensitivity to glucose with decreasing size due to an increase in active sites. Further sensitivity can be added by building up thickness of material on a conductive substrate and including a percolating network to facilitate electron transport.

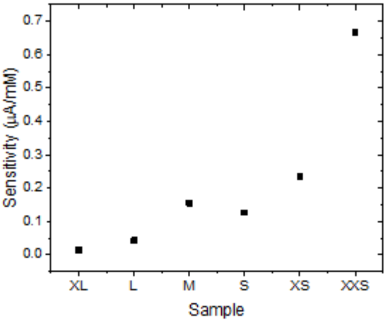

Figure 1 Sensitivity to Glucose of copper hydroxide nanosheets dropcast on glassy carbon electrodes

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Strain-induced localization of interlayer excitons in a van-der-Waals heterostructure

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Interlayer excitons (IX) in van-der-Waals heterostructures are currently subject to intense study [1-4]. For example, they constitute an interacting Bosonic system in the solid state whose properties can be widely tuned by electric fields [1], the choice of materials and/or the microscopic separation and rotational alignment of the individual layers [2-4].

Here, we trap a small number of IX in a potential formed through local strain and investigate the interaction of those IX with each other through dipole-dipole interaction. Hereby, we place a WSe_2-$MoSe_2$-heterobilayer onto a dielectric substrate patterned with arrays of 130nm (diameter) × 90nm (height) nano pillars, using viscoelastic stamping (Fig. 1a).

Outside the pillar region, confocal photoluminescence measurements performed at low temperature (10K), reveal clear IX emission around 1.37eV (see Fig 1b) [1], that blue shifts, as expected, by ~50 meV upon increasing the excitation level over six orders of magnitude from 10^{-1} to 10^{5} W/cm^{2} [5]. In contrast, on top of the pillar sites, the IX emission for the lowest excitation levels studied is accompanied by sharp lines that emit about ~50-80meV below the IX peak (see Fig. 1c). We attribute these sharp emission lines to localized IXs (LIX in fig 1 c). Upon increasing the laser power, characteristic multiexciton - like emission emerges; emission lines discretely appear at higher energies with increasing pump power. We identify these sharp emission features as arising from multiple, interacting IX localized within a local strain potential. Our results are consistent with a model describing dipolar exciton-exciton interactions within a realistic strain-induced potential.

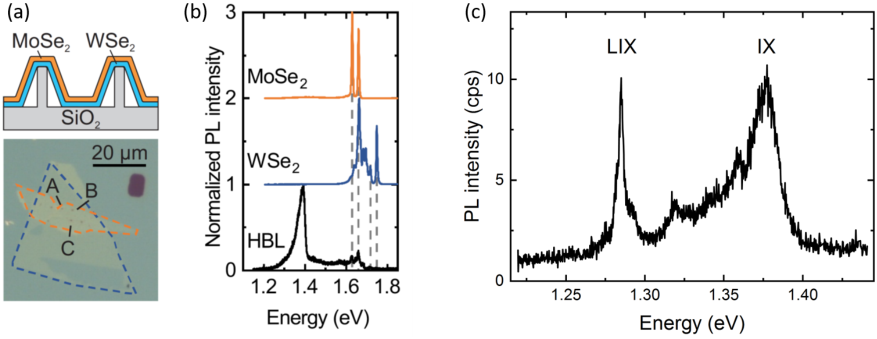

FIG. 1. (a) Schematics of the sample used in this work. A heterobilayer of WSe_2 and $MoSe_2$ is placed on top of a SiO_2 substrate patterned with nano pillars leading to local strain gradients. Optical micrograph of the sample used in this work. The monolayers of WSe_2 and $MoSe_2$ are outlined with blue and orange dashed lines, respectively. The nano pillars appear as dark dots in the heterobilayer region. (b) Typical low temperature photoluminescence of the monolayers and the heterobilayer (HBL) outside the pillar region. (C) Typical photoluminescence spectrum on top of a nano pillar showing discrete and sharp emission from strain localized interlayer excitons (ILX).

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Poster-Th11

Interlayer excitons in stacked TMDC heterostructures

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We computed the theoretical bandstructures and absorption spectra of bilayer $MoSe_2$-WSe_2 and MoS_2-WSe_2 heterostructures with different stacking orders by solution of the excitonic Bethe-Salpeter equation with GW corrections [1] and inclusion of spin-orbit-coupling. We find two spin-orbit split Rydberg series of low oscillation strength and a surprisingly large binding energy below the absorption onset of the monolayer materials, which arise from a type-II alignment of the monolayer bands. Together with the indirect electronic band gap of the heterostructures, our results confirm the recent experimental observation of a doublet nature of the interlayer photoluminescence. We further show that the local stacking order leads to small variations in the hybridization between the $MoSe_2$ and WSe_2 bands and has a decisive effect on the polarization dependence of the interlayer excitonic absorption [2]. Our results motivate detailed studies of electron-phonon coupling effects and exciton dynamics in TMDC heterostructures by time-resolved optical experiments and *ab initio* methods.

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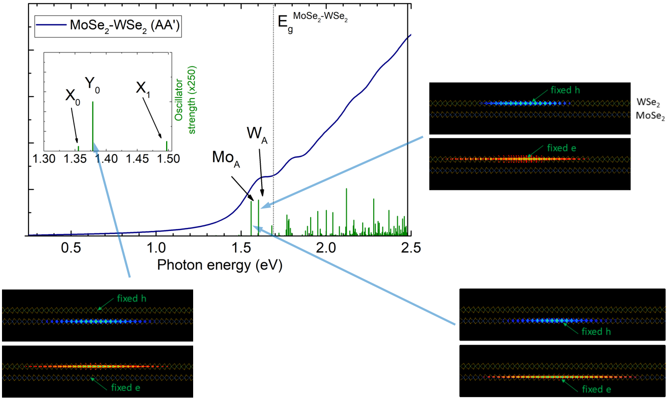

FIG. 1. *Simulated absorption spectrum of AA'-stacked $MoSe_2/WSe_2$ heterostructure. Plots of the excitonic wavefunctions of selected excitonic transitions are shown. The electronic (hole) parts of the wavefunctions for a fixed hole (electron) position are depicted in blue (red).*

Germanane and its derivatives for catalytic application

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Abstract

In these days, environmental pollution is an ever growing problem and pursuit for easy and low-cost technologies for pollution treatment is increasing. Many novel materials suitable for pollution treatment and environment remediation occurred in the last two decades. Following the boom of graphene discovery, many two-dimensional (2D) nanomaterials like layered transition metal dichalcogenides, phosphorene and MXenes have attracted a great deal of scientific attention. Furthermore, covalently terminated group IV of graphane analogues, i.e. silicane, germanane and stannanane, also belong to this family of 2D nanomaterials. However, properties and potential application of these materials are far less explored compared to the above-mentioned nanomaterials.

Germanane (Ge_6H_6) with buckle structure is usually prepared by etching of calcium layers by hydrochloric acid from $CaGe_2$ to yield H-terminated germanane [1,2]. Another synthetic possibility is a reaction of $CaGe_2$ with halogenated organic molecules. According to the structure of the organic molecules, a wide variety of different functional groups can be attached on the surface of germanane. These functionalizations bring up the possibility to prepared many germanane derivatives with various properties tailored to the specific application. Thus, electronic structure and band gap of germanane can be easily tuned by surface modification. Photocatalytic properties of germanane and its derivatives were tested in application like hydrogen generation from catalytic hydrolysis of ammonia under visible light irradiation or photocatalytic decomposition of organic pollutants [3,4].

In this work, we utilize germanane and its derivatives as materials for photocatalytic degradation of organic pollutants (*e.g.* organic dyes), photocatalytic decomposition of explosive residuals (*e.g.* picric acid and trinitrotoluene) and as catalysts for hydrogenation/oxidation reactions in organic chemistry. We focused on the comparison of H-terminated germanane with those materials modified by various organic molecules in the performance of above-mentioned application. Our results uncover the possible utilization of germanane in environment remediation application.

Acknowledgement

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Modified Germanane for Electrochemical Sensing

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In the last decade, graphene and its derivatives have obtained a lot of attention due to their unique properties such as ballistic transport, high transparency or large surface area. However, graphene has also some drawbacks such as zero bandgap or high chemical stability that limits its applications in microelectronics and its possible modifications, respectively. Nowadays, inorganic analogues of graphene (silicene and germanene) are intensively studied in terms of fundamental properties, applications and possibility of modifications. Silicene and germanene have very similar electronic structure and their charge carriers are also massless Dirac fermions as in the case of graphene.[1] Unlike planar graphene, these analogues prefer buckled structure in which lower and upper atoms are not the same when a vertical electric field is applied.[2] Thus, bandgap can be easily triggered by application of external electric field. Therefore, silicene and germanene have a great advantage towards utilization in microelectronics such as field effect transistor.[2] Beside application of electrical field, the bandgap could be tailored also by lateral size, strain or covalent and noncovalent modifications.[2-3]

The covalent modifications of 2D nanomaterials are one of the most fashionable way to tailor their properties and for passivation of their surface.[4] Up to this day, only few articles were published about functionalization of germanene surface. Most of them deals with functionalization by hydrogen or methyl group.[5] Similarly to hydrogenation of graphene, a hydrogenation of germanene leads to the bandgap opening and fully hydrogenated germanene is called germanane.[5b] Germanane possesses sp^3 hybridization which leads towards intense adsorption of gas or vapour molecules. Adsorbed species can dramatically influence an electronic structure which can lead to specific response of a sensor.[6] Previously reported theoretical calculations have shown the possible application of germanane as a chemical sensor or biosensor for various species.[6-7] However, no such practical work has been published yet to the best of our knowledge.

Here, we want to present preparation of germanane which was modified by organic residues with electron withdrawing or donating groups. Synthesis of modified germanane was based on selective etching of calcium from $CaGe_2$ with in situ modification by various organic residues. These residues were different in length of their chain as well as type of functional group within their structure. Thus, different inductive effects of covalently bonded residues affected electron structure of modified germananes. Prepared materials were placed on interdigitated electrodes, on which were tested for electrochemical detection by impedance spectroscopy. Our results suggested usability of modified germanane towards detection of various volatile organic compounds.

Acknowledgment

This work was supported by the Czech Science Foundation (GACR No. 19-26910X).

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Poster-Th14

Contacts to 2D materials with vanishing Schottky barriers by NanoFrazor lithography

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Forming high-quality electrical contacts is a key issue in fabricating high-performance 2D material electronic devices. However, predominant fabrication processes (i.e. electron beam lithography followed by metal evaporation and lift-off) typically yield poor quality non-ohmic metal contacts with high Schottky barriers and large contact resistances [1]. Here, we show that NanoFrazor (thermal scanning probe) lithography that relies on thermal decomposition of polymer resists [2] can be used to pattern high-quality metal contact electrodes to monolayer MoS_2 with high reproducibility, sub-10-nm resolution, and a throughput comparable to high-resolution electron beam lithography [3]. The approach offers simultaneous in situ imaging and patterning as well as superior markerless alignment accuracy [4] and does not utilize high-energy charged particle beams. We developed a variety of lift-off metallization processes with different resists and solvents achieving gaps between metal electrodes below 10nm. Using this technique, we have patterned both top-gated and back-gated field-effect transistors with metal electrodes in direct contact with monolayer MoS_2. These devices exhibit vanishing Schottky barrier heights (around 0 meV, Figure 1), record-high on/off ratios of 10^{10}, no hysteresis, and subthreshold swings as low as 64 mV per decade without the use of negative capacitors or hetero-stacks.

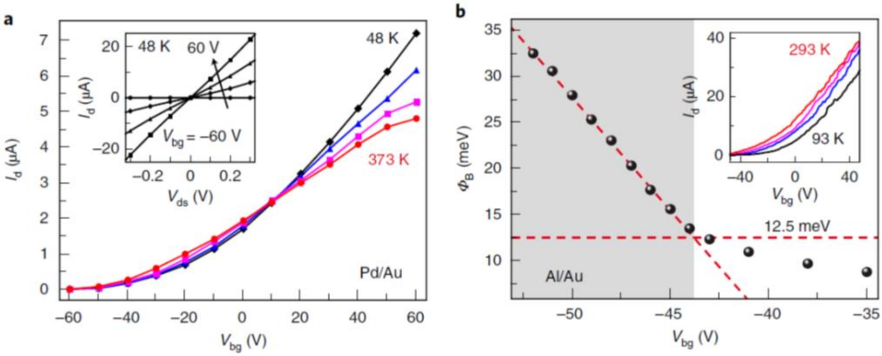

FIG. 1. Schottky barrier height (SBH) characterization of NanoFrazor patterned FETs with exfoliated monolayer MoS_2.
a) Temperature-dependent transfer curves with Pd/Au contacts (V_{ds} = 0.1 V). Inset: corresponding output curves of the same device at 48 K. b) Gate voltage dependence of SBH with Al/Au contacts (V_{ds} = 2 V). The deviation from the linear response at low V_{bg} (dashed red line) defines the flat band voltage and the SBH. Inset, corresponding temperature-dependent transfer curves (V_{ds} = 2 V). Figures from reference [3].

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Poster-Th15

Spin polarization in monolayer semiconductors by magnetic proximity coupling

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Layered ferromagnet-semiconductor heterostructures have proven ripe systems for both advanced spintronics research and real-world applications in information technology. The highly ordered states inherent to ferromagnets, alongside their strong collective responses to external electromagnetic fields, makes them ideal candidates to enable control of charge and spin in closely proximitized semiconductors. Monolayers of $MoSe_2$ are atomically thin direct band-gap semiconductors which combine a regime of coupled spin and valley physics with an optically bright exciton ground state. As such, they are highly promising in the development of valleytronics, an analogue of spintronics which utilizes the carrier valley degree of freedom as an information carrying pseudospin. Crucially, $MoSe_2$ is also associated with robust chiral optical selection rules, efficiently bridging the gap between spin-valley polarization and optical addressability. By bringing TMD monolayers into contact with ferromagnetic materials, it becomes possible to bestow an additional, valley, degree of freedom onto the magnetic proximity coupled system.

Here, a monolayer of $MoSe_2$ is transferred directly on top of a 10nm thick film of europium sulfide (EuS), a ferromagnetic insulator with a rock-salt crystal structure. The reflectance contrast spectrum from the sample displays two absorption resonances ascribed to attractive and repulsive polarons (Fig. 1a), associated with interactions between a photogenerated exciton and the electron Fermi sea [1]. The EuS film strongly modifies the magneto-optical response of the TMD monolayer, leading to a 100% degree of circular polarization of the attractive polaron under an external magnetic field of B = 8T (Fig. 1a), indicating complete spin polarization of conduction band electrons [2]. Furthermore, the valley splitting of the repulsive polaron is strongly enhanced by the EuS magnetic exchange field (Fig. 1b), and follows a non-linear curve characteristic of the magnetization response of the ferromagnetic film, indicating uninhibited proximity coupling between the two materials [3]. This work highlights the potential of ferromagnet-semiconductor heterostructures based on 2-dimensional materials towards the full realization of valleytronics.

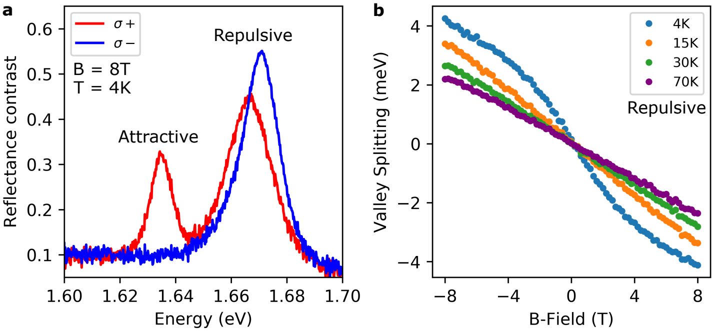

FIG. 1. *(a) Reflectance contrast, defined as* $(R_0 - R)/R_0$ *where* R_0 *and* R *are the reflectance of the substrate and monolayer regions, respectively, from the sample under an external magnetic field of* $B = 8$ *T and a temperature of* $T = 4$ *K. Red (blue) curves indicate* $\sigma^+(\sigma^-)$ *light polarization. The higher (lower) energy absorption resonance is the repulsive (attractive) polaron. (b) Valley splitting* $E(\sigma^+) - E(\sigma^-)$ *of the repulsive polaron as a function of external magnetic field and sample temperature. The valley splitting is enhanced when the sample is below the Curie temperature of EuS.*

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Photochemical Modifications of Few-Layered Grey Arsenic

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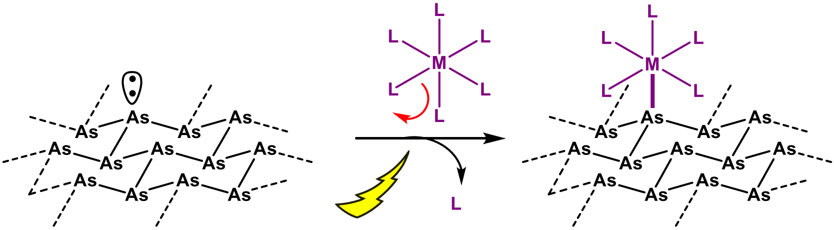
Functionalization of mono-elemental layered materials is one of the greatest challenges in current material research.[1] Among them, elements from the 15th group of the periodic table, pnictogens, play an important role as they can overcome or improve properties of graphene, for example, they have direct band gap in monolayer (or few-layer) form. Besides black phosphorus, grey arsenic represents a promising candidate for the application in new (opto)electronic devices, as sensors or (electro)catalysts. So far, the chemistry of pnictogens is mainly based on non-covalent modifications,[2] where pnictogen lone pairs interact with large molecules, for example, perylenes or fullerenes.

Compared to non-covalent modification, direct attachment of a functional group can result in better control of properties. Unfortunately, a simple synthetic pathway for modification of exfoliated grey arsenic does not exist yet except modification with carbenes.[3] This issue is limiting the application of layered grey arsenic because of its instability under ambient conditions. Here is presented covalent functionalization of layered grey arsenic with photolabile metal complexes, which form a donor-acceptor bond to the grey arsenic sheet (**Scheme 1**). As a result, it is possible to tune the electronic properties of layered arsenic as well as modify the catalytic properties by the attached metal. Moreover, the stability of the modified exfoliated arsenic is enhanced.

Acknowledgements: This work was supported by the Czech Science Foundation (GACR No. 19-17593Y).



Scheme 1. Photomodification of few-layered grey arsenic with metal complexes.

[1] M. Pumera, Z. Sofer, *Adv. Mater.* **2017**, *29*, 1605299.
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Poster-Th17

In-situ Doping of Black Phosphorus for Potential Applications

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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.

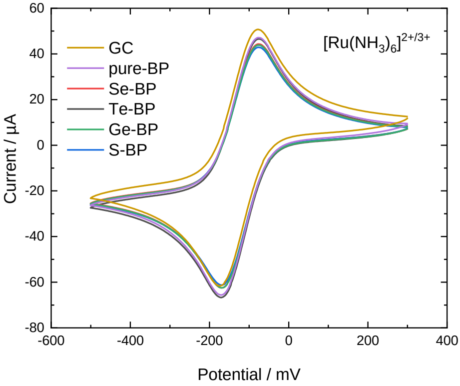

FIG. 1. Cyclic voltammpgram (vs. Ag/AgCl) of bare glassy carbon (GC) compared with pure and doped black phosphorus modified GC in $Ru[(NH_3)_6]^{2+/3+}$ redox couples (10 mM), scan rate: 100 mV s^{-1}.

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This work was supported by the Czech Science Foundation (GACR No. 19-26910X).

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Poster-Th18

Time- and momentum-resolved valley exciton distribution in bulk WSe$_2$

Shuo Dong, Samuel Beaulieu, Michele Puppin, Christopher W. Nicholson, Maciej Dendzik, Tommaso Pincelli,
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Transition metal dichalcogenides semiconductors feature exceptional optoelectronic properties like strong excitonic interactions [1] and spin-valley polarization associated with optical excitation [2]. The investigation of excited states in k-space provides access to optically-bright as well as dark states on equal footing. Here, we perform the time-resolved excited-state mapping of the excited states in the entire first Brillouin zone in bulk WSe$_2$ using four-dimensional time- and angle-resolved photoemission spectroscopy. Time-of-flight momentum microscopy, measuring the electron momentum distribution in both in-plane directions simultaneously, in combination with a XUV laser source at 500 kHz repetition rate [3], enables the study of valley carrier dynamics with 30 fs temporal resolution.

Upon resonant excitation, the excited states scatter from the K valleys to the global conduction band minima in the Σ valleys, consistent with previous work [4]. We measure the time-dependent distribution of the excited state during the electronic relaxation due to electron-phonon interaction. In particular, we analyze the shape of the excited states in the Σ valleys and initially observe an elliptical momentum distribution. By mapping the exciton distribution in k space, it is possible to descript the characters of the exciton wave function in real space, including the exciton size and the corresponding orbital of state. Simultaneously, the band gap narrows by a similar amount as the exciton binding energy. Furthermore, we discuss the time-dependent 2D momentum distribution of the excited state signal in terms of signatures of the electron-hole interaction of excitonic states.

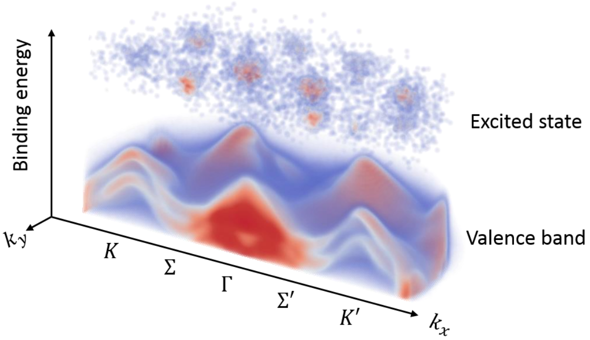

FIG. 1. 3D Brillouin zone mapping of WSe2. The band dispersions along K- Σ - Γ - Σ'- K' and spin orbital splitting of valence band at K points are well-resolved. The exciton distribution in the conduction band indicates the global minima at Σ valley. The intensity of excited state is enhanced for clarification.

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Photochemical Modifications of Few-Layered Grey Arsenic

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Functionalization of mono-elemental layered materials is one of the greatest challenges in current material research.[1] Among them, elements from the 15th group of the periodic table, pnictogens, play an important role as they can overcome or improve properties of graphene, for example, they have direct band gap in monolayer (or few-layer) form. Besides black phosphorus, grey arsenic represents a promising candidate for the application in new (opto)electronic devices, as sensors or (electro)catalysts. So far, the chemistry of pnictogens is mainly based on non-covalent modifications,[2] where pnictogen lone pairs interact with large molecules, for example, perylenes or fullerenes.

Compared to non-covalent modification, direct attachment of a functional group can result in better control of properties. Unfortunately, a simple synthetic pathway for modification of exfoliated grey arsenic does not exist yet except modification with carbenes.[3] This issue is limiting the application of layered grey arsenic because of its instability under ambient conditions. Here is presented covalent functionalization of layered grey arsenic with photolabile metal complexes, which form a donor-acceptor bond to the grey arsenic sheet (**Scheme 1**). As a result, it is possible to tune the electronic properties of layered arsenic as well as modify the catalytic properties by the attached metal. Moreover, the stability of the modified exfoliated arsenic is enhanced.

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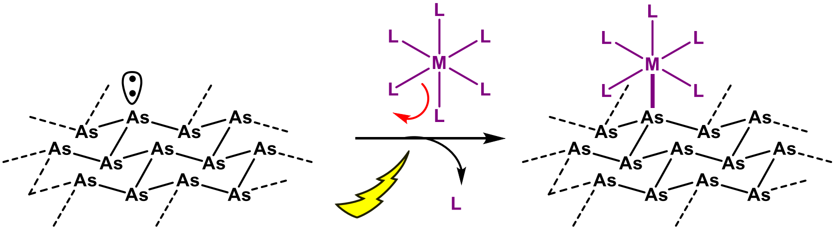

Scheme 1. Photomodification of few-layered grey arsenic with metal complexes.

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[2] M. Marcia, A. Hirsch, F. Hauke, *FlatChem* **2017**, *1*, 89-103.
[3] J. Sturala, A. Ambrosi, Z. Sofer, M. Pumera, *Angew. Chem. Int. Ed.* **2018**, *57*, 14837-14840.

Electronic band structure of mixed TMDs $Mo_{1-x}W_xSe_2$ compounds determined experimentally.

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Robert Kudrawiec,[2] Teodor Gotszalk[1]

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Indirect and direct band gaps in $Mo_{1-x}W_xSe_2$ (molybdenum tungsten diselenide alloys) were examined with the use of photoacoustic (PA) and photoreflectance (PR) spectroscopy. Investigated samples had the following compositions: x = 0, 0.014, 0.19, 0.37, 0.51, 0.71, 1. Bulk crystals were obtained from 2D semiconductors. Whereas atomically thin samples were prepared by mechanical exfoliation (scotch tape method). It was possible to apply the micro-photoreflectance experiment for atomically thin samples due to their lateral size of around 10 μm.

It was shown that the PA technique allows to determine the indirect band gap, while, not sensitive to indirect transitions, the PR method effectively determines direct optical transitions.
The energies of indirect (I) and direct (A, B and C) excitonic transitions were determined from the measurements carried out on bulk material. The energy of excitonic transitions A and B was also determined in two-dimensional samples and compared with the results of photoluminescence.
The energies of the observed transitions (I, B and C) in bulk samples obey with Vegard's law quite accurately and does not require the bowing parameter to be taken into account.
In addition, we performed KPFM measurements of monolayers to determine the work function of each material.

Poster-Th21

Germanane – Versatile Precursor Towards Functionalized Germananes

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Boom in two-dimensional (2D) materials has been started by the rediscovery of graphene, mono-elemental 2D carbon allotrope. Since then, a lot of other 2D materials has been introduced, for example, layered black phosphorus, arsenic and antimony as representatives of mono-elemental 2D materials or MXenes, metal oxides or transition metal dichalcogenides as layered compounds. The heavier analogues of graphene based on silicon or germanium have also been predicted, but they cannot be prepared from bulk elements by simple mechanical exfoliation as for example graphene from graphite. Moreover, pure monolayers of silicon or germanium (called silicene or germanene, respectively) have been prepared only by "bottom-up" procedure by deposition on suitable substrates (for example, Al(111)). Fortunately, the modified germananes can be prepared by chemical exfoliation from layered Zintl phases where two layers of germanium are separated by suitable metal, for example $CaGe_2$. Treatment of such material with an acid leads to hydrogenated analogue of germanene – germanane[1] – with general formula Ge_6H_6, or treatment with primary alkyl iodides lead to alkylated germananes.[2] Unfortunately, the published procedure works the best only for liquid alkyl iodides but more hindered or aromatic substituents are not attached by this protocol and the procedure requires huge excess of alkylating reagent.

In this communication, we would like to present novel synthetic protocol based on functionalization of germanane, which is readily obtained by simple acidic exfoliation. This material represents an ideal platform for further derivatization because it is easily obtained in high yields without the need for expensive reagents. The idea is based on the formation of nucleophilic germanium by deprotonation of Ge-H grouping followed by the addition of electrophilic reagent (**Scheme 1**). This procedure accepts not only primary alkyl halides but also more hindered alkyl halides, aryl halides and other electrophilic compounds. By this approach, $Ge_6H_xR_{6-x}$ are formed, therefore, the electronic properties can be finely tuned according to the current need.

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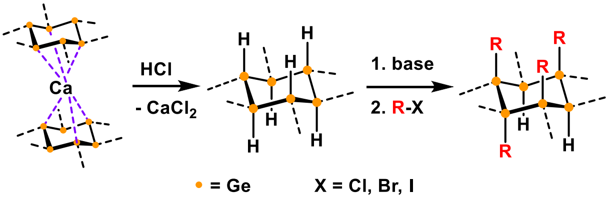

Scheme 1. Protocol for modification of germanane by an alkyl halide.

Acknowledgement: This work was supported by the Czech Science Foundation (GACR No. 19-17593Y).

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Poster-Th22

Liquid phase promoted growth of large area WS2 flakes

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Monolayer and few layer transition metal dichalcogenides (TMDs) attract significant attention due to interesting semiconducting and optoelectronic properties, however, complete picture of their growth proccess is still lacking.

Recently, methods using NaCl as a growth promotor became popular. NaCl is thought to act in two ways: by forming volatile transition metal (oxy)chlorides that can easily reach growth substrate and by forming eutectic sodium compounds on the substrate. Using our miniature CVD system with optical access, we directly observe sequence of events during growth of WS2 from sodium rich precursors directly deposited on SiO2/Si substrate. Melting of precursors with partial wetting of substrate gives way to pseudo-partial wetting regime after start of sulfurization. During early stages of flake growth there is coexistence of the visible liquid phase and growing flakes. Mass transport of precursor phase toward growing edges is seen. Growing flakes, tens of microns in size, can sometimes slide over substrate indicating that they are supported by liquid layer during growth ("rheotaxy"). Liquid layer below WS2 is directly visible if thicker, and can be seen promoting growth of bi/multilayers that can grow to tens of microns. Disappearance of visible liquid phase leads to slowdown and end of growth. Merging dynamics is also observed. Unlike MoS2 where joining of flakes is usually smooth, WS2 tends to “crumple” leading to multilayer formation and subsequent growth. Clean merging is occasionally seen. Grown flakes, that can reach few hundred microns in size, are further characterized with AFM, SEM, Raman spectroscopy and PL to confirm their thickness and quality . In the end, we discuss relevance of our findings to proposed mechanisms of TMDs growth.

Poster-Th23

Raman spectroscopy of chemically and mechanically functionalized MoS_2

Narine Moses Badlyan,[1] Nina Pettinger,[1] Xin Chen,[2] Wanzheng Zhang,[2] Kathrin Knirsch,[2] Andreas Hirsch,[2] and Janina Maultzsch[1]

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Transition metal dichalcogenides (TMDCs), such as MoS_2, are of great interest due to their large surface, which offer the opportunity to tune their electrical and optical properties especially the nature of their interaction with the environment by covalent functionalization.
Here, we present a spectroscopic study of MoS_2 flakes prepared by mechanical exfoliation and MoS_2 films grown by chemical vapor deposition (CVD), functionalized with organic molecules. We discuss the effect of excitation laser power as well as of the temperature on the Raman spectra, and compare them to those of functionalized MoS_2 powder samples of several sizes.

Ultrathin metal halide flakes as a versatile platform to study intercalated compounds

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Two-dimensional (2D) semiconducting materials are among all the 2D families the most studied due to their suitability for different electronic and optoelectronic applications [1]. Metal halides is a family of layered semiconducting materials that have gained interest when used as precursors in their bulk form for the synthesis of perovskite solar cells [2]. One example is ammonium lead iodide layered perovskites, which have been used in solar cells [3]. The procedure for obtaining these compounds from metal halides is through intercalation of the salt ions in the metal halide grid.

In this work, we synthesize PbI_2 flakes [4] in order to study the intercalation of different ammonium salts. The PbI_2 flakes were measured optically and optoelectronically. Once the PbI_2 samples are characterized, we intercalate them by evaporation of methylammonium lead iodide, ethylammonium lead iodide and propylammonium lead iodide. This simple method for obtaining complicated 2D compounds from a different 2D material is very powerful for the study of intercalated nanomaterials.

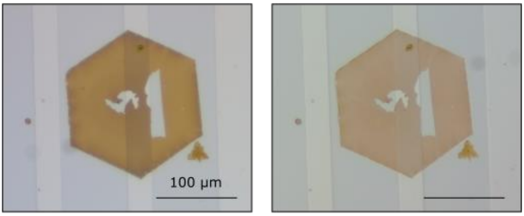

FIG. 1. Optical images of a photodetector of PbI_2 (left) and the same device after the intercalation with ethylammonium lead iodide.

[1] Koppens F., Mueller T, Avouris P, Ferrari A, Vitiello M and Polini M. *Nat. Nanotechnol*. 9 780–93 (2014).
[2] Manser J S, Christians J A and Kamat P V. *Chem. Rev.* 116 12956–30 (2016).
[3] Dou L *et al.*, *Science*, vol. 349, no. 6255, pp. 1518–21 (2015).
[4] R. Frisenda *et al. Nanotechnology*, vol. 28, no. 45, 2017.

Poster-Th25

Excitonic valleytronic devices based on TMDCs

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Interlayer excitons in van der Waals heterostructures of transition metal dichalcogenides (TMDCs) are of great interest due to their unique spin-valley and moiré physics. These aspects could be implemented to realize next-generation photonic and valleytronic devices, as well as exploring new physical phenomena. For example, one could imagine to encode information in the excitons valley-state, which could be then transported using polarized light. Indeed, the fact that excitons can be manipulated electrically but couple naturally to photons offers an advantageous combination with potential for relevant technological applications. Moreover, thanks to the high binding energy of excitons in TMDCs, such excitonic devices can work up at room temperature [1], making them a strong candidate for the realization of practical valleytronic devices. In this talk, we will demonstrate electrical manipulation of interlayer excitons in van der Waals heterostructures. By application of electric and magnetic fields, we will show that different types of device operations can be realized, achieving control over the transport, polarization and wavelength of interlayer valley-excitons [2]. The ability to effectively control the motion and properties of interlayer excitons is a significant step forward towards new device concepts which do not rely on electric charges.

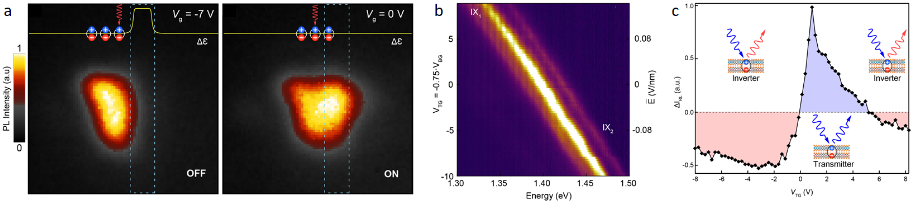

FIG. 1. *a) Excitonic transistor in the OFF and ON state. b) Tuning of the interlayer exciton energy by application of electric fields. c) Polarization switch based on interlayer excitons*

[1] Ciarrocchi A., Unuchek D. *et al.* Nature Photonics, **13**, 2, (2019)
[2] Unuchek, D., Ciarrocchi A. *et al.* Nature, **560**, 7718, (2018)

Poster-Th26

The Raman Spectroscopic Characterization and Transport Measurements on exfoliated flakes of $Pb_{0.77}Sn_{0.23}Se$ topological insulator

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The considerable accomplishments in the graphene studies have rendered a renaissance of interest in other layered materials, especially those that benefit from the topological crystalline insulator states. This study aims to elaborate on the phonon properties of $Pb_{0.77}Sn_{0.23}Se$ flakes with thickness spanning from several micrometers to the nanometric limit obtained by mechanical exfoliation from the bulk by performing Raman scattering spectroscopy. We have explored its electronic behavior by fabricating Hall bar devices and performing magneto-resistance Hall measurements to confirm the topological behavior. Our results reveal that the Raman data of this material has a thickness dependency (**Figure 1**) associated with the plasmon enhanced electron-phonon coupling. The temperature dependence of longitudinal resistance (R_{xx}) confirms the results obtained by Ch. Zhang *et al.* [1] in thin films grown by molecular beam epitaxy. The thin flakes of this material exhibit an insulating behavior for temperatures below 90K and semiconducting behavior for temperatures above 90K (**Figure 2**) explained by the strong Coulomb interactions.

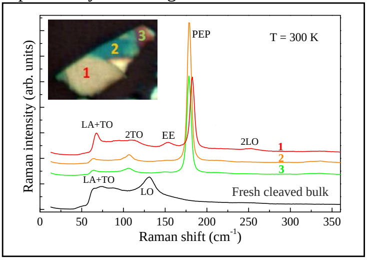

Figure 1: Raman spectra of $Pb_{0.77}Sn_{0.23}Se$ flakes in three different positions; position 1 is ~ 140 nm thick, position 2 is ~120 nm thick, position 3 is ~100 nm thick; the surface modes at 180 cm^{-1} are ~ 5 times more intense than the 130 cm^{-1} bulk mode of the bulk crystal.

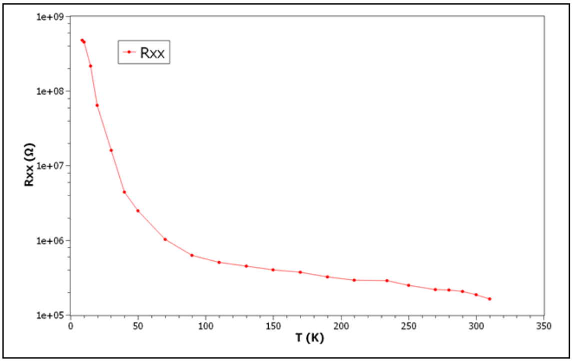

Figure 2: Temperature dependent resistance of the $Pb_{0.77}Sn_{0.23}Se$ thin film with a nominal thickness of 130nm.

[1] C. Zhang *et al.*, Nano Letters **15**, 2161 (2015).

Poster-Th27

Ultra-long working distance spectroscopy of single nanostructures with aspherical solid immersion micro-lenses

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T. Kazimierczuk,[1] A. Rodek,[1] J. Suffczyński,[1] P. Wasylczyk,[1] and P. Kossacki[1]

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Standard experimental setup for spectroscopic studies of single semiconductor nanostructures requires an microscope objective in front the studied sample. In order to avoid photon losses the numerical aperture (NA) of used microscope objective should be as high as possible. On the other hand longer distance from the sample to the light collecting optics (working distance, WD) is often desirable. It is particularly important in systems with restricted access to the sample, e.g., in case of split-coil superconducting magnets. Commercially available microscope objectives with magnification 100x has NA=0.6 for WD=8 mm, which is not sufficient for all applications.

In this work we present aspherical micro-lenses which redirects emitted photons from semiconductor nanostructure into light cone of NA=0.025 - the outcoming light can be collected by 1 inch-diameter lens at the distance of 590 mm from the sample. Resulting working distance is more than 70 times longer than the one offered by conventional microscope objectives.

Micro-lenses were fabricated by two-photon polymerization direct laser writing (TPP-DLW). This technique allows for three dimensional printing of micro objects made of transparent non-conductive resin that withstands cryogenic temperatures [1]. The resin after polymerization has refractive index n=1.52 which is intermediate value between higher refractive index of semiconductor and much lower refractive index of air. As a result, one also obtain an increase in photon extraction efficiency due to reduction of internal reflection of light in semiconductor.

We demonstrate usability of the proposed solid immersion lenses with monolayers of transition metal dicalcogenites (TMDs), in particular $MoSe_2$ and WSe_2 ($\lambda \approx 790$ nm and $\lambda \approx 760$ nm respectively). We have observed more than a hundred-fold increase in collection efficiency in spectroscopic setup with NA < 0.025. The lenses were also tested with single self-assembled CdTe/ZnTe quantum dots ($\lambda \approx 600$ nm) containing single manganese and cobalt ions. Finally, we show that our solution works at shorter wavelength with single CdSe/ZnSe quantum dots ($\lambda \approx 500$ nm), thus confirming the feasibility of broadband operation of fabricated lenses.

Presented micro-lenses could be especially useful for single nanostructure spectroscopy in very high magnetic fields - due to the absence of metal elements as well as in microwave cavities or optical dilution refrigerator systems.

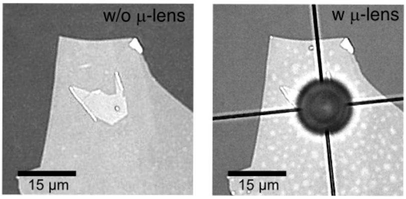

FIG. 1. *Monolayer of $MoSe_2$ coverd with hBN before (left) and after fabrication of microlens (right).*

[1] A. Bogucki *et al.* Opt. Express **26**, 11513 - 11518, (2018)

Optical, electrical and electro-optical properties of MS_2 (M= Mo,W) nanotubes

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Band structure calculations as well as some optical and electrical properties of MS_2 (M=Mo, W) nanotubes were published already two decades ago and provided important insight into their electronic and optical behavior. Alongside the recent progress in the synthesis of pure phases of such multiwall tubes, their optical and electrical characterization has advanced considerably, lately. Using optical extinction measurements, strong coupling between optical cavity modes confined in the core of the nanotubes and the A and B excitons, was observed in WS_2 nanotubes with average diameter of 120 nm.[1] It was recently realized that this phenomenon is limited to nanotubes with diameter exceeding 80 nm. Nanotubes of smaller diameter are unable to confine such cavity modes in their core, and their optical behavior is consistent with pure excitonic absoprtion.[2] Furthermore, microluminescence measurements revealed that gallery whispering modes exist in MoS_2 tubes with diameter exceeding 300 nm.[3] They manifest themselves as periodic overtones in the photoluminescence spectrum of such tubes. In another series of works, ambipolar transistor behavior and electroluminescence were observed in WS_2 nanotubes gated with ionic liquids.[4] More recently, evidence for strong bulk photovoltaic effect was brought forward, which was attributed to the loss of inversion symmetry and time reversal symmetry in the chiral tubes.[5] These studies and others to be discussed, show that multiwall MS_2 nanotubes present a platform for revealing rich and hitherto unexplored physics.

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1. L. Yadgarov et al., *Phys.Chem.Chem.Phys*. **20**, 20812 (2018).
2. S.S. Sinha, submitted.
3. D.R. Kazanov et al., *Appl. Phys. Lett*. **113**, 101106 (2018).
4. Y.J. Zhang et al., *2D Mater.* **5**, 035002 (2018).
5. Y.J. Zhang et al., *Nature*, in press.

Moiré Intralayer Excitons in a $MoSe_2/MoS_2$ Heterostructure

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Spatially periodic structures with a long range period, referred to as moiré pattern, can be obtained in van der Waals bilayers in the presence of a small stacking angle or of lattice mismatch between the monolayers. Theoretical predictions suggest that both intra- and interlayer excitons in van der Waals heterobilayers experience a modulation of the potential of the order of tens and hundreds of meV, respectively, in the presence of a moiré pattern. This yields optically active states with different energies, which can be viewed as an elegant way to tailor the properties of a material by simply overlapping another material with a commensurate crystal structure [1].

In our work, we investigate the effect of the moiré pattern on the intralayer excitons of $MoSe_2$ in a hBN encapsulated $MoSe_2/MoS_2$ heterostructure for the first time [2]. Across the whole area of the heterostructure, we observed consistently a double peak in both the PL and absorption spectra of the intralayer exciton of $MoSe_2$, as shown in Fig. 1(a,b). The additional peak is blue shifted by ~10meV with respect to the main exciton transition, which is a value consistent with theoretical predictions [1]. By performing temperature dependent PL spectroscopy, we reveal that the high energy satellite peak vanishes at temperatures around 90K, giving an activation energy to the main exciton PL transition of ~25meV, again in line with theoretical predictions [1]. Circularly polarized PL spectroscopy, summarized in Fig. 1(c,d), demonstrates that the high energy peaks are co-polarized with the main excitonic transitions, confirming that the moiré pattern does not influence the circular dichroism of intralayer excitons. This can be explained noting that the rotational symmetry of the transitions does not change in the plane of the monolayers, which is in contrast with the expected behavior of interlayer excitons.

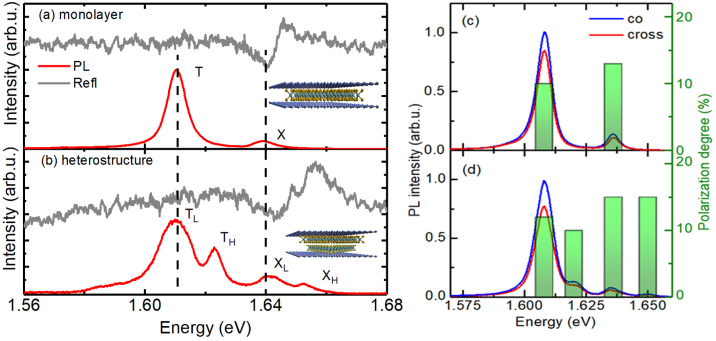

Figure 1. PL (red) and absorption (grey) spectra of (a) an isolated $MoSe_2$ monolayer and of (b) $MoSe_2$ monolayer overlapping with MoS_2, showing the effect of moiré pattern. Circular dichroism in (c) an isolated $MoSe_2$ monolayer and in (d) $MoSe_2$ monolayer with moiré side bands.

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[1] Fengcheng Wu, *et al*, Physical Review Letters **118**, 147401 (2017).
[2] Nan Zhang, *et al*, Nano Letters **18**, 7651−7657 (2018).

Poster-Th30

Electrostatic control of exciton flux in van der Waals heterostructures

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[2]*Institute of Materials Science and Engineering, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland*
[3]*National Institute for Materials Science, 1-1 Namiki, Tsukuba 305-0044, Japan*

Large exciton binding energy in recently discovered two-dimensional semiconductors makes exciton physics accessible even at room temperature in these materials. Particular interest has been given to the interlayer excitons in van der Waals heterostructures based on transition metal dichalcogenides (TMDCs) with type-II band alignment. Whereas individual two-dimensional materials have short exciton diffusion lengths, the spatial separation of electrons and holes in different layers in heterostructures increases exciton lifetime and thus helps to overcome this limitation. In addition, this charge separation realizes built-in out-of-plane electric dipole moment, allowing exciton manipulation via an external electric field, showing promise for next-generation photonic devices relying on excitonic effects. Here, we present van der Waals devices made of TMDCs heterostructures encapsulated in h-BN with graphene control gates, which allow us to manipulate exciton dynamics by creating electrically reconfigurable potential profiles for the exciton flux. Our excitonic device demonstrates electrically controlled transistor actions up to room temperature, that holds great promise for realizing small and efficient interconnects between optical data transmission and electrical processing systems.

Poster-Th31

High Quality Single and Few-layered $ReSe_2$ Synthesized by Chemical Vapor Transport

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In the past few years, transition metal dichalcogenide (TMDCs) have attracted intensive attentions in nanoelectronic devices and optoelectronic devices. Compared with isotropic TMDCs, anisotropic TMDCs show lower symmetry and thus exhibit anisotropic electrical and optical properties in plane. The most representative anisotropic TMDC are ReS_2 and $ReSe_2$, which form quasi-1D Re chains in the basal plane[1-2]. However, the controllable synthesis of two-dimensional 1*T*'-$ReSe_2$ with high quality remains a challenge. Here, we developed a convenient and controllable method for the synthesis of high quality's $ReSe_2$ based on chemical vapor transport (CVT). By using different transfer agents, $ReSe_2$ varied degrees of anisotropy can be obtained. By regulating the growth time and temperature, we can reduce the thickness from bulk to monolayer with length about 10 μm. The field-effect transistors (FETs) fabricated with the as-grown $ReSe_2$ show n-type semiconducting behavior with a current on/off ratio of 10^5 and a charge carrier mobility up to 4.98 $cm^2 \cdot V^{-1} s^{-1}$, indicating the high quality of the obtained flakes. Our approach paves the way for exploring the applications of high quality $ReSe_2$ in novel electronics and optoelectronics.

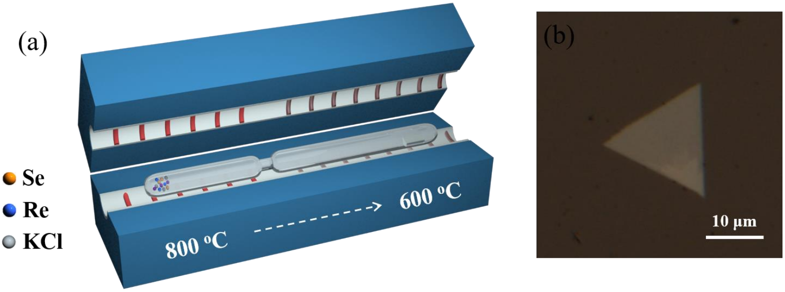

FIG. 1. (a) CVT growth diagram of $ReSe_2$, Re powder and Se powder are served as the source materials and KCl is as a transport agent. (b) Typical morphology of few-layer $ReSe_2$ flakes grown by CVT with KCl.

[1] Erfu Liu et al. Nat. Commun., 5, 3252, (2014)
[2] Etienne Lorchat et al. ACS. Nano, 10, 2752, (2016)

Poster-Th32

Electron-phonon coupling in layered 2D halide perovskites

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Gaëlle Trippé-Allard,[2] Damien Garrot,[3] Emmanuelle Deleporte,[2] and Paulina Plochocka[1]

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Strong electron-phonon coupling in hybrid perovskites is the underlying mechanism of some of their unique properties such as the unusual charge-carrier dynamics and the broadening of emission lines. The electron-phonon interaction in these materials is dominated by coupling to LO phonons via the Fröhlich interaction. Two-dimensional layered perovskites are characterized by large exciton binding energies on the order of hundreds of meV due to quantum and dielectric exciton confinement. As a consequence, excitons dominate their photophysical properties even at room temperature and 2D perovskites provide an interesting platform for studying exciton dynamics and their coupling to the phonon bath.

We performed spectroscopic studies of the layered Ruddlesden-Popper perovskite $(C_6H_5C_2H_4NH_3)_2PbI_4$ (PEPI). Recently, the fast growth of PEPI monocrystalline thin films has been demonstrated [1]. We investigated thin PEPI films synthethized using this technique and observed simultaneous changes in photoluminescence and transmission as a function of temperature. In agreement with a previous study [2] at low temperatures we observed periodically spaced spectral features, which we assigned to phonon replicas. The energetic spacing of the features of around 40 meV corresponds to the energy of a phonon located on the phenyl group of the organic spacer involving rotation of the NH_3 and phenyl moieties [2]. Significant changes in the spectral shape could be seen at around 18 K and 70-90 K. The change of the spectral character above 70 K is probably related to the formation of a polaronic exciton at low temperatures [2]. We analyzed the relative intensity of the spectral features at low temperatures to conclude about the strength and nature of the electron-phonon coupling. To further elucidate the nature of the transitions, we performed magneto-optical measurements. The energies of the main excitonic line and of the two periodic spectral features shift with the same rate under magnetic field. This confirms the assignment of the additional features as phonon replicas.

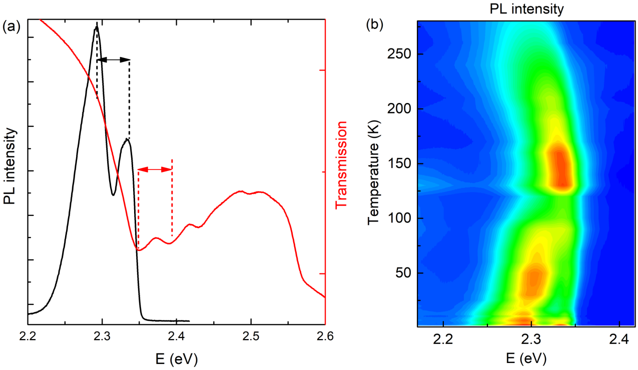

Figure 1. *(a) Photoluminescence (black) and transmission (red) spectra of a thin PEPI film measured at 6 K. The energy separation of the main excitonic peak and the first phonon replica is marked for both spectra. (b) Temperature dependence of the photoluminescence intensity.*

[1] F. Lédée *et al.* CrystEngComm, **19**, 2598, (2017)
[2] D. B. Straus *et al.* J. Am. Chem. Soc., **138 (42)**, 13798-13801 (2016)

Poster-Th33

The interplay between the direct and indirect excitonic quasiparticles in $MoS_2/MoSe_2$ heterostructure probed by temperature-dependent photoluminescence

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Stacking of transition metal dichalcogenide (TMD) monolayers into heterostructures emerged as a new possibility to modify the optoelectronic properties of their constituent layers. Although excitons in monolayer TMDs provide a rich platform to study the internal quantum degrees of freedom of electrons, the subpicosecond radiative lifetime, resulting from the very large dipole moment, strongly limits their applications in practical valleytronic devices. To overcome this limitation TMDs-based on vertically-stacked heterostructures has been introduced, where consecutive layers are bound by relatively weak van der Waals (vdW) forces. The possibility to combine different layers of TMDs produces an extra degree of freedom to tailor the properties of vdW structures. These structures exhibit type II band alignment where electrons and holes are spatially separated, forming an interlayer exciton. The spatial separation of electron and hole wave-functions reduces the oscillator strength leading to a significant increase of the recombination lifetime. Interlayer excitons also follow the same valley optical selection rules, however, the reduced spatial overlap of the charged carriers results in a long-lived valley polarization which is beneficial for valleytronic applications.

As the van der Waals heterostructures are relatively new there are still many open questions which shows that the overall understanding of their physics is still very limited. Recent photoluminescence (PL) studies have revealed complex structure of interlayer exciton with varying selection rules or lifetimes [1]. According to a simple band structure model [2] of TMDs stacks the nontrivial structure of interlayer exciton might originate from the phonon-assisted **k**-indirect transitions between the Λ and K points of the Brillouin zone.

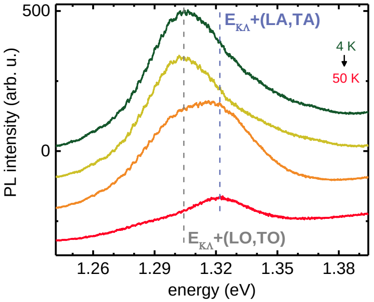

FIG. 1. Temperature dependence of the interlayer exciton photoluminescence. The observed double-structure corresponds well with the energies obtained from the simulations of the band structure of the MoSe2/MoS2 bilayer.

Here we present an investigation of a $MoS_2/MoSe_2$ heterostructure encapsulated in hBN. The structure under investigation exhibits a PL signal related to both the neutral exciton and trion at 1.62 and 1.60 eV, respectively, as well as a low-energy signal located at ~1.3 eV attributed to interlayer exciton emission. The temperature resolved studies (Fig. 1) revealed a complex structure of the interlayer exciton: at low temperature of 4 K the PL signal is dominated by a pronounced emission at 1.3 eV. With increasing temperature an additional transition on the high energy side becomes visible (~1.32 eV). At the temperature of ~35 K the intensity of both transitions equalizes, and further increase of temperature leads to a substantial reduction of the PL peak intensity of the main transition. Band structure simulations show the Λ valley is the lowest conduction valley of the bilayer. As a result the optical signals at ~1.3 and 1.32 eV correspond to the **k**-indirect transitions between the Λ (conduction) and K (valence) valleys with the assistance of optical and acoustic phonons, respectively.

[1] A. Ciarrocchi et al., Nat. Photonics **13**, 131 (2019)

[2] A.T. Hanbicki et al., ACS Nano **12**, 4719 (2018)

Poster-Th34

Exciton-Exciton Annihilation in Two-dimensional Halide Perovskites at Room Temperature.

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Ruddlesden-Popper 2D halide perovskites (RPPs) are a promising material for optoelectronics application such as solar cells, light-emitting devices and photodetectors. [1,2] Besides, they present a better stability than their 3D counterpart. RPPs formed natural quantum well structures, where the perovskite layer is intercalated between large organic cations. We have studied the exciton recombination dynamics at room temperature in pure phase crystals of PEA-based RPPs (PEA=phenylethylammonium $C_6H_5C_2H_4NH_3^+$) $(PEA)_2(CH_3NH_3)_{n-1}Pb_nI_{3n+1}$ (n=1, 2, 3 and 4) (Figure 1) using time-resolved photoluminescence with a large range of power excitations. We observe the presence of an increasing fraction of out-of-equilibrium free carriers as the number of perovskite layers increases on a picosecond timescale just after photoexcitation. The emission mechanism is then defined by the recombination of excitons with long lifetime spanning on several tens of nanoseconds. In the low excitation regime, the photoluminescence dynamics is non-exponential due defect-assisted recombination. In the high excitation regime, below the Mott transition, traps are saturated and many body interactions becomes important. As observed in other 2D materials, Exciton-Exciton Annihilation is then the dominant recombination path. The results shed light on the origins of non-radiative losses in RPPs, which should be addressed to optimize the efficiency of future optoelectronic devices.

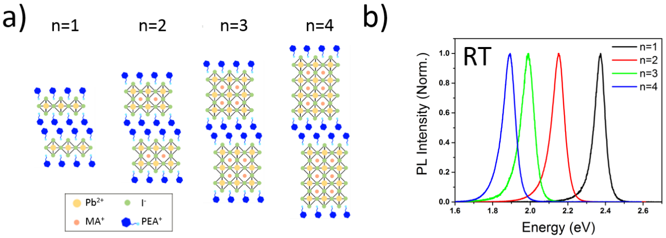

Figure 1 : Schematic representation of RPPs structures of (PEA) 2 (MA) n Pb n I 3n+1 (n=1, 2, 3 and 4) b) Room temperature photoluminescence spectra of RPP crystals from n=1 to 4

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Poster-Th35

Exciton localization in $MoSe_2$ monolayers induced by adsorbed gas

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Lattice defects and dielectric environment play a crucial role for 2D materials. In particular an effect related to the extreme surface-to-volume ratio is the huge influence of physisorption and chemisorption of gas molecules on the optical and electronic properties [1]. In this work we investigate the impact of physisorbed air gas molecules on the optical properties of $MoSe_2$ monolayers by means of low-temperature photoluminescence (PL). More specifically we focus on the physics of excitons localized by gas molecules studying the effects of laser irradiation and temperature.

Laser irradiation has the effect to relieve the monolayer surface of the physisorbed gas molecules which causes the disappearance of the localized exciton peak and the appearance of the trion peak. The effect is completely reversible in air (figure 1a).

The localized exciton PL peak shows a systematic and large red-shift with temperature (figure 1b). This energy shift cannot be explained only in terms of bandgap renormalization. Instead we explain the shift in terms of thermal instability of the localized excitons in combination with hopping effects between localization centers.

Furthermore we have performed a careful lineshape fitting of the PL spectra. A key point of the fitting model is that we introduce an effective temperature in the form $T_{eff}^2 = \alpha T^2 + T_0^2$ in order to take into account the inhomogeneous disorder potential induced by defects and physisorbed gas molecules (figure 1c). In the previous formula, T is the lattice temperature, T_0 is an induced temperature at zero Kelvin, and α is a fitting parameter. With this model we are able to reproduce with excellent agreement the experimental data [2].

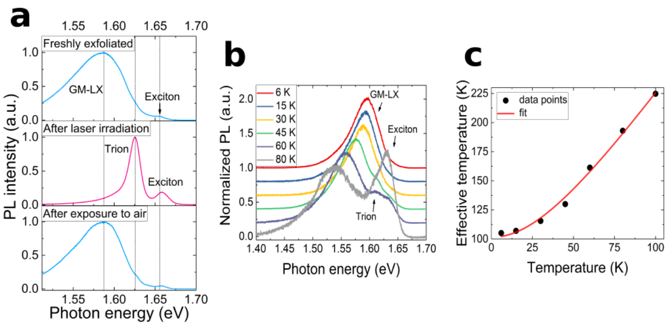

FIG. 1**.** (a) PL spectra at 5 K of $MoSe_2$ monolayer before and after laser irradiation. (b) Temperature dependence of the air gas molecules localized exciton (GM-LX) peak. (c) Effective temperature extracted from the model vs. the actual lattice temperature.

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Poster-Th36

Straining twisted bilayers of transition metal dichalcogenides

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Monolayer transition metal dichalcogenides (TMDs) are promising materials for future 2D electronic and optoelectronic systems and their main and most stable representatives molybdenum disulphide (MoS_2) and tungsten disulphide (WS_2) have been widely studied. [1] However, monolayers can be stacked to build materials that have never existed before where their properties depend not only on the order of the layers but also on the relative twisting angle between atoms in the subsequent layers to the extent of having either superconducting or insulating electronic properties depending on the angle of stacking. [2,3] In order to develop flexible devices based on 2D materials it is necessary to investigate strain and angle dependence of bilayer homo and hetero structures of transition metal dichalcogenides.

Main focus of this research is investigation of optical properties under uniaxial straining of different stacking orders of bilayer tungsten disulphide which is grown by chemical vapour deposition process and transferred to the appropriate surfaces (substrates). Experimental result of measured absorption, photoluminescence and Raman spectra are further verified by theoretical modelling results which are in good agreement with experimental results.

Optical response of strained and twisted bilayers is dominated by excitonic effects and phonon coupling. Lattice deformation influences the stacking order and induces change in the local electronic structure which is observed as a shift in energy of the spectrum and populations of neutral and charged excitons as well as change in exciton-phonon coupling.

To take full advantage of the electronic and optical properties of transition metal dichalcogenides and their Van der Waals layered structures, it will be necessary to control the local electronic structure, on which the effect of lattice deformation is significant. [4]

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Poster-Th37

Printing MXene Supercapacitors in *2D* and *3D* on the *Micro*- and *Macro*-Scale

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The ever growing demand for electrical energy in compact and wearable devices calls for new approaches towards fabrication of lightweight and flexible energy storage systems. Micro supercapacitors (MSCs) can meet those requirements if produced on flexible substrates. $Ti_3C_2T_x$ MXenes have been demonstrated to perform particularly well as material for electrodes and current collectors of MSCs [1]. Oxide surface terminations cause a strong pseudocapactive behaviour, which enabled planar devices on paper with high areal capacitance values of $\sim 61\, mF\, cm^2$ [2]. The synthesis of $Ti_3C_2T_x$ yields colloidal dispersions of monolayer nanosheets in water, rendering device fabrication *via* printing a highly feasible method.

We have studied the printing of $Ti_3C_2T_x$ based MSCs via various different techniques, i.e. stamping and rolling using 3D printed stamps, as well as direct extrusion-, inkjet- and aerosol-jet printing [2, 3]. This suite of processes enables the fabrication of MSCs on arbitrary substrates across several orders of magnitude both in their dimensions and also their specific capacitance. The smallest lateral feature sizes of MSCs produced are on the range of tens of micrometres, while the largest devices cover several cm^2. The produced film thickness can be as low as very few sheets stacks on the order of tens of nanometres when employing inkjet printing on one hand, on the other, aerosol-jet printing allows the fabrication of 3D printed structures with vertical sizes up to millimetres. We will review and compare the different printing techniques in respect to the resolution, scalability, device performance and impact on material characteristics.

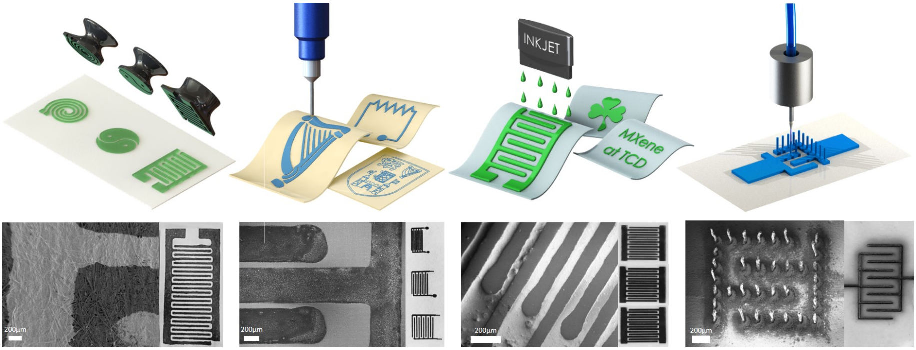

FIG. 1. *Schematic drawing of stamping, extrusion-, inkjet- and aerosol-jet printing (top). Photographs and SEM images of devices produced by said techniques (bottom).*

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