

Rigid valence band shift due to molecular surface counter-doping of MoS₂

D. Nevola, B.C. Hoffman, A. Bataller, H. Ade, K. Gundogdu, D.B. Dougherty*

Department of Physics, North Carolina State University, Raleigh, North Carolina 27695, United States



ABSTRACT

Adsorption of the acceptor material tetracyanoquinodimethane can control optoelectronic properties of MoS₂ by accepting defect generated excess negative charge from the surface that would otherwise interfere with radiative decay processes. Angle Resolved Photoelectron Spectroscopy measurements show that the MoS₂ band structure near the Γ point shifts rigidly upward by ~ 0.2 eV for a complete surface coverage of acceptor species as expected for an upward Fermi level shift due to charge transfer to the TCNQ. The molecular adsorbate orbitals visible in photoemission are indicative of an anionic species, consistent with interfacial charge transfer but without evidence for hybrid states arising from covalent adsorbate-surface interactions. Thus, our interface studies support the notion that molecular adsorbates are a useful tool for controlling optoelectronic functionality in 2D materials without fundamentally modifying their favorable band structures.

1. Introduction

Single layer transition metal dichalcogenides like MoS₂, WS₂, and others have shown intense photoluminescence that makes them the crucial optoelectronic materials in the new 2D materials paradigm [1]. The goal in this field is layer-controlled assembly of heterostructures using 2D building blocks (graphene, transition metal dichalcogenides (TMDC's), hexagonal BN, topological insulators, etc). This requires careful attention to controlling interfaces and interfacial interactions.

Surface transfer doping [2] of the TMDC MoS₂ with molecular films can drastically alter its optoelectronic properties by compensating electrostatic potential modifications due to defects [3–6]. In MoS₂, excess electrons from sulfur vacancy defects bind to excitons within the material creating a lower energy trion state [7]. Trion formation hinders optoelectronic properties such as photoluminescence (PL) [3], and photoconductivity [8] due to its lower energy and high effective mass respectively. Molecular film growth is a method of controlling the formation of trions at the surface, and has demonstrated the ability to tune the PL of single layer MoS₂ [3]. More specifically, molecular acceptor films increase the PL intensity while molecular donor films decrease it [3]. Ridding the surface of excess electrons through acceptor p-doping inhibits the formation of trions since there are fewer electrons to interact with existing excitons. Conversely, donor films add electrons and increase the rate of trion formation. Importantly, naturally occurring sulfur vacancy defects give rise to an unintentional n-doping effect in MoS₂, making trion formation an intrinsic challenge in this material [7,9,10]. As a result there is a significant need to understand and quantify strategies for molecular doping control and how they can be integrated into the 2D materials paradigm.

We explore the fundamental modifications of MoS₂ band structure

to understand the mechanisms behind surface doping with molecular adsorbates of tetracyanoquinodimethane (TCNQ). The valence band structure of MoS₂ has been extensively studied by both theoretical calculations [11–13] and experimental studies [12–14]. Its bright PL in the monolayer limit is due to a direct transition occurring at the K point in the first Brillouin zone, with the direct optical gap having a value of 1.88 eV [15]. Upon the addition of more layers, the gap becomes indirect with a value of 1.29 eV [16]. The band structure remains virtually unchanged in the vicinity of the K point. The gap becomes direct when the valence band maximum (VBM) at the Γ point increases towards the Fermi level and the conduction band minimum (CBM) approximately halfway between the gamma and K point decreasing towards the Fermi level [11,17]. Han et al. experimentally verified that the valence bands near the maximum at the Γ point are due to the out of plane d_z^2 electrons and those near the maximum at the K point are formed from the in-plane d_{x-y}^2/d_{xy} bands [14]. This agrees with the layer dependence of the bands because the addition of more layers decreases the electron confinement in the out of plane direction by introducing the attractive, interlayer van der Waals interaction.

Since the van der Waals interaction between layers in bulk MoS₂ is relatively weak, it is clear that the MoS₂ band structure can be very sensitive to noncovalent perturbations. For example, introducing slight strain in the lattice can control the location of the VBM at the Γ point [18]. The impact of noncovalent molecular adsorption may also be very significant in the context of the extreme sensitivity of MoS₂ band structure. We need to address whether bands are distorted by molecular adsorbates or simply shifted by interfacial charge transfer.

It was predicted that the weak interactions between TCNQ molecules and substrate result in a band structure consisting of a superposition of the bands of each with those of MoS₂ shifted towards the

* Corresponding author.

E-mail address: dbdoughe@ncsu.edu (D.B. Dougherty).

Fermi level [10,19]. Although calculations place the former lowest unoccupied molecular orbital (F-LUMO) slightly above the VBM of MoS₂, the possibility for band overlap remains since it depends on the exact magnitude of the shift and the location of the TCNQ orbitals, which are also known to vary. [10,19,20]. Additionally, the increased adsorption energies at the sulfur vacancy sites may result in re-normalization of defect energy states, as well as an induced spin splitting of energy states [10]. These theoretical considerations give insight into the band structure change with the addition of molecular dopants, and motivate our experimental study.

In this paper, we quantify the effects of surface doping MoS₂ through adsorption of the molecular acceptor tetracyanoquinodimethane (TCNQ). We utilize angle resolved photoemission spectroscopy (ARPES) to observe the changes in band structure through a stepwise deposition of TCNQ. Our ARPES measurements show a rigid band shift saturating at ~ 0.2 eV. We further demonstrate charge transfer by observing the orbitals of TCNQ, which are then compared to theoretical studies. Our observations are consistent with theoretical calculations and can be used to further understand the doping affects of TCNQ on MoS₂.

2. Experimental methods

Bulk 2H-MoS₂ crystals were purchased from SPI supplies. Band structure measurements were performed in an ultra-high vacuum (UHV) chamber (base pressure $\sim 2 \times 10^{-10}$ mbar) using a Specs UVS 10/35 He I (21.2 eV) light source and a Phoibos 150 hemispherical analyzer equipped with a 2D CCD detector. All samples were cleaved in air with adhesive tape prior to loading into the UHV chamber and were annealed in-situ at 425 °C for 3 hours. To check the surface quality and verify the crystal orientation, low energy electron diffraction (LEED) and ARPES were performed on all crystals prior to molecular deposition. All depositions and subsequent measurements were carried out with the sample at room temperature. Surface charging was accounted for in all photoemission spectra by a rigid shift of bands to match the valence band photoelectron spectra in reference 15.

Powdered 7,7,8,8-tetracyanoquinodimethane (TCNQ) was purchased from Sigma Aldrich and loaded as received into a quartz crucible in a thermal evaporator. Stepwise TCNQ growth was performed using organic molecular beam deposition (OMBD) in high vacuum (10^{-6} mbar) in a chamber attached to the ARPES chamber. Deposition rate was monitored using a quartz crystal microbalance.

3. Results and discussion

The MoS₂ substrates were first characterized using LEED to verify the surface quality and orientation. Fig. 1(a) shows the LEED pattern obtained with an electron beam energy of 167 eV, which verifies the hexagonal lattice structure of MoS₂. The momentum dispersing direction of our 2D photoelectron detector is along the vertical direction of the LEED image, and so we observe the band structure along the Γ -K direction. The clean MoS₂ band structure is shown in Fig. 1(b). These ARPES measurements agree with previously reported band structures, with the VBM occurring at the Γ point in the bulk crystal [13,17].

Upon TCNQ deposition, we observed the band structure of MoS₂ shifted towards the Fermi level as shown in Fig. 2(a), indicative of a p-doping effect. Additionally, we see that this is a rigid shift, uniform throughout the band map. Thus, the surface doping affects all valence electron orbitals uniformly. In addition, the bands near 4 eV consist of the Mo 4d in-plane orbitals, the same orbitals that make up the VBM near the K point [14]. Therefore, since the electronic make up at the optically active, high k portion of the Brillouin zone is of similar origin to the bands in our measurements, we expect a rigid shift of equal value at high momenta, which is not shown in the ARPES maps in Fig. 2(a), due to angular range of the photoelectron spectrometer.

If there were a strong electronic mixing interaction between the

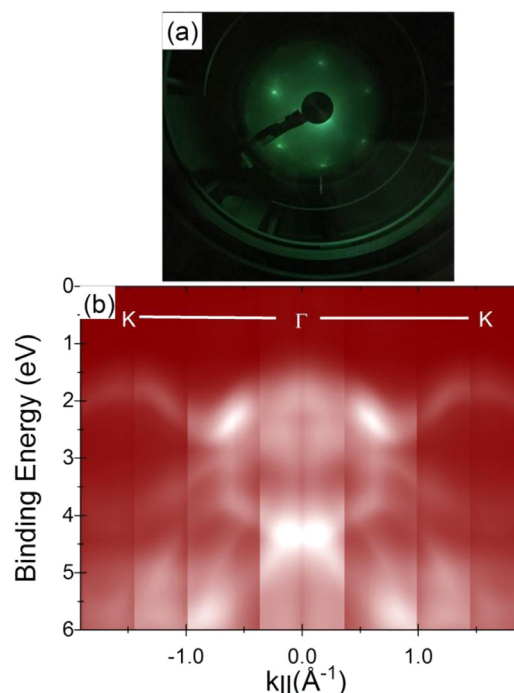


Fig. 1. (a) LEED image for bulk 2H-MoS₂ crystal depicting the orientation in the Γ -K direction as lined up with the 2D detector used for ARPES. (b) ARPES map of bulk 2H-MoS₂ along the Γ -K direction. The ARPES map was measured from Γ -K and then symmetrized.

molecule and substrate, we would expect it to act as a perturbation in the z-direction, and have a notable impact near the Γ point [18]. Therefore, this rigid band shift indicates an essentially noncovalent interaction (i.e. without formation of hybrid interface states involving mixing of substrate and molecular orbitals) between the TCNQ molecules and the MoS₂ crystal surface [19]. It should then be noted that optical transitions at any points in the Brillouin zone are affected equally and can also be used to assist in explaining changes in device performance due to the surface doping with TCNQ. Our measurements show the effect of molecular acceptor layers in tuning the Fermi level in MoS₂ as employed in optimizing photoluminescence efficiency [3]. Increasing the TCNQ growth time leads to an eventual saturation after a ~ 0.2 eV shift, consistent with theoretical calculations [10,19].

Next, we analyze the energy bands of TCNQ on the MoS₂ surface to characterize the charge transfer from MoS₂ to TCNQ. To do this, we subtract the MoS₂ photoelectron spectrum before growth (0 sec growth, Fig. 2a) from the spectrum after growth (7 sec growth, Fig. 2c). In order to perform this subtraction, the substrate spectrum was shifted in energy to compensate for the Fermi level shift as a result of the TCNQ-induced charge transfer. The curves were then normalized to the local minimum at ~ 1.7 eV in between the two uppermost bands of MoS₂. The substrate photoemission curve was then subtracted from the growth curve. The line profiles taken at the Γ point (after shifting and normalization for the film-deposited spectrum) before subtraction are presented in Fig. 3(a). The subtracted spectrum is shown in Fig. 3(b). We observed a weak change of shape to the spectrum after deposition as should be expected because (1) the coverage is only a monolayer and (2) there is a strong energy overlap between the bands of MoS₂ and the orbitals of TCNQ [20]. After subtraction, we observed the presence of three distinct peaks, which are reminiscent of the anionic species TCNQ⁻ but not consistent with charge neutral TCNQ. This assignment is based on the spacing between the three peaks as described in detail below.

The lowest energy feature is the former lowest unoccupied molecular orbital of neutral TCNQ (F-LUMO, i.e. the highest occupied

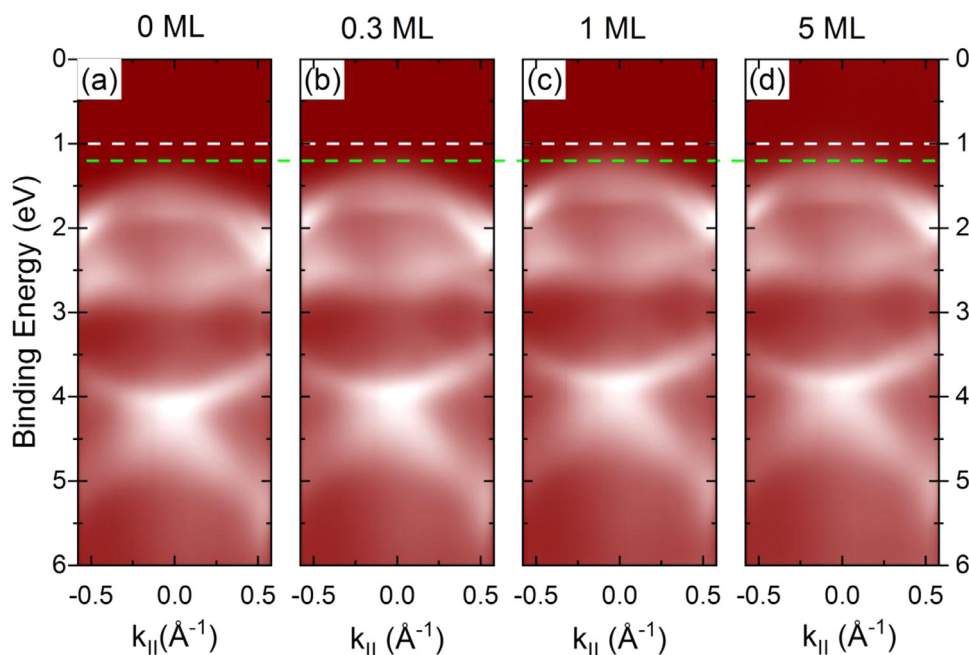


Fig. 2. ARPES map of MoS₂ as a function of increasing TCNQ growth beginning with a clean substrate (left) and ending with a band shift saturation (right). The green dashed line indicates the position of the VBM as in the left plot and the white dashed line indicates the position of the VBM as in the right plot.

molecular orbital (HOMO) of TCNQ⁻). The next two peaks arise from the former HOMO and former HOMO-1 of the neutral TCNQ species. Since the absolute positions of these peaks are expected to vary depending on the doping concentration [20], we focus on their relative positions, which allows a definitive assignment of the TCNQ adsorbates as negatively charged. The measured difference between the F-LUMO and the F-HOMO is 0.9 eV, and between the F-HOMO and F-(HOMO-1) is 1.7 eV, which compares well with previous photoemission studies of anionic TCNQ⁻ [20,21] created by co-deposition with alkali metals.

Theoretical calculations place the LUMO of TCNQ 0.25 eV above the VBM of monolayer MoS₂ [10,19]. We observed the location of the F-LUMO embedded within the uppermost part of the valence band spectra. This is also in agreement with the DFT calculations when considering that the VBM of MoS₂ shifts up by 0.3 eV in its transition to the bulk [17]. Thus, the presence of this state indicates charge transfer occurring between the molecule and substrate. Were charge transfer to not occur, the HOMO of TCNQ would be at a binding energy of 2.77 eV [20], and there would be no features at lower binding energy. Through the addition of an electron, the LUMO is brought down below the Fermi

level and the HOMO is shifted up towards the Fermi level, yielding the two states at the aforementioned locations [20,21]. The electrons which are transferred from the surface of MoS₂ are most likely excess electrons due to defects in the form of sulfur vacancies [9]. The change in surface potential thus results in the rigid band shift evident in Fig. 2.

We expect that the charge transfer occurs strictly within the surface layer of MoS₂. In our measurements, this is seen by the saturation of the VBM shift after the formation of 1 monolayer. Furthermore, optical absorption studies involving molecular films on top of multilayered MoS₂ show a drastic decrease to the molecular film-induced changes to the spectrum with an increase in the number of MoS₂ layers. More specifically, the exciton emission is less quenched by surface dopants for increasing numbers of MoS₂ layers in the substrate [5]. While this could be due in part to the switch to an indirect gap, it is more plausible that it is because optical absorption in multilayered MoS₂ is a surface *and* bulk measurement, and the spectrum becomes more overwhelmed with absorption from the less doped deeper layers as the sample gets thicker. It also implies that TCNQ does not interact with MoS₂ much deeper than a surface layer. This makes sense when considering weak

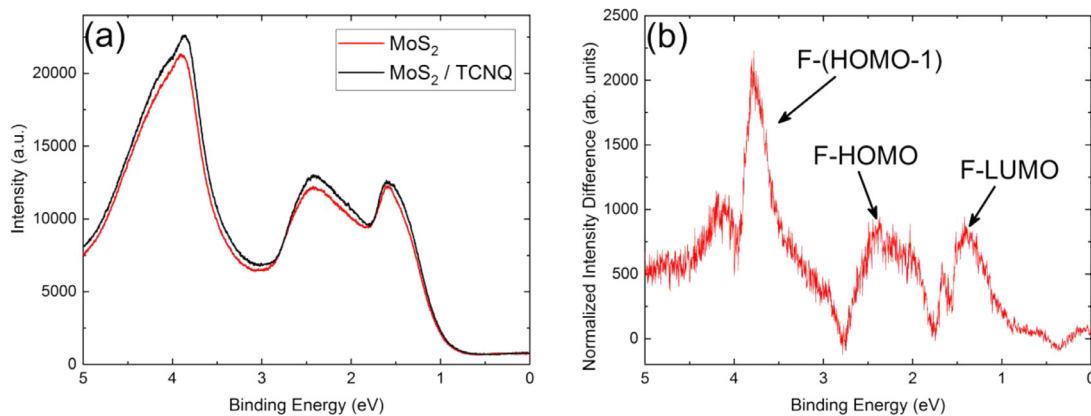


Fig. 3. (a) The energy distribution curves at the gamma point for both the bare MoS₂ and the final growth. (b) The difference in photoemission spectra between the two curves in (a). The energy difference between the F-LUMO and the HOMO-1 was calculated to be 0.9 eV, and between the F-HOMO and F-(HOMO-1) was calculated to be 1.7 eV.

Table 1

Summary of TCNQ doping effects on the band gap shift observed in our experiment, applied to both bulk and monolayer MoS₂. E_{neutral} is defined as half of the energy gap, or the location of the Fermi level on a defect-free sample, and E_{F} is the Fermi level.

	Bulk MoS ₂	Monolayer MoS ₂
Band Gap	1.29 eV[16]	1.88 eV[15]
$E_{\text{F}} - E_{\text{neutral}}$ (before doping)	0.55 eV	0.81 eV[17]
$E_{\text{F}} - E_{\text{neutral}}$ (after doping)	0.35 eV	0.61 eV

molecule-substrate coupling combined with interlayer screening effects [22]. Due to the exceptionally low inelastic mean free path of electrons at energies close to 21.2 eV [23], we fully expect that the measured electrons in our measurements are mostly from the surface interaction with TCNQ. Thus, our results can be extended to predict the full doping effect on monolayer MoS₂.

We now proceed to summarize our key quantitative results, which are also displayed in table 1. The VBM of clean MoS₂ is 1.2 eV below the Fermi level. By taking the indirect gap of bulk MoS₂ to be 1.29 eV [16], we verify that the substrate is intrinsically n-doped. Accounting for the observed 0.2 eV shift, we find that the MoS₂ still contains excess electrons, but that the system is 0.2 eV closer to being charge neutral due to the surface layer of TCNQ. Previous measurements on monolayer MoS₂ place the Fermi level at 1.75 eV above the VBM [17]. Performing the same analysis using the bandgap of monolayer MoS₂ to be 1.88 eV [15], we obtain a strong intrinsic n-doping of ~ 0.6 eV still present after our observed shift of 0.2 eV is accounted for. Here, we stress that our experimentally observed shift in the bulk is remarkably similar to theoretical calculations using monolayer MoS₂ [10,19]. The spectral weight of the trion peak in PL measurements is miniscule compared to as-prepared MoS₂ [3], indicating the high efficiency of trion suppression as a function of Fermi level location with respect to mid gap.

Finally, we quantify the molecular level effect of doping with TCNQ by considering the relative magnitude of excess electron density to the expected molecular density of a saturated layer of TCNQ. The unintentional n-doping of the clean MoS₂ crystal arises from sulfur-vacancy defects [24] that contribute 2 excess electrons. We use $3.5 \times 10^{13} \text{ cm}^{-2}$ for the defect density as determined by scanning electron microscopy so that the excess electron density on the surface is $\sim 7 \times 10^{13} \text{ cm}^{-2}$ [24]. To estimate the area density of the TCNQ molecules in the first layer, we consider the close packed “orthogonal” structure discussed in Ref [25] as representative of a typical saturated monolayer with an area per unit cell of 67.72 Å². This leads to a molecular density of $1.5 \times 10^{14} \text{ cm}^{-2}$, which is the same order of magnitude as the estimated excess electron density.

A more quantitative analysis of charge transfer effects has been addressed by computational studies [10,19]. It is found that there is only partial charge transfer to the TCNQ adsorbates on MoS₂. This fact explains why the surface doping we report here does not fully compensate the defect-induced doping even though the estimated density of excess electrons is substantially lower than the density of molecules. It also explains why the use of the higher electron affinity surface dopant F₄-TCNQ is more efficient at removing excess electrons from single layer MoS₂ [3]. Evidently, more charge is transferred per molecule in that case.

Our work provides the basic quantitative interface characterization underpinning molecular doping control of optical properties of MoS₂. The general strategy of molecular doping is increasingly employed to control MoS₂ properties. For example, phthalocyanine has been used to control photo-induced electron transfer [26]. Benzyl viologen [5] provides surface n-doping that quenches excitons in single-layer MoS₂. In addition to optical properties, MoS₂ electrical device properties such as contact resistance and transistor threshold voltage can also be controlled by the polymer polyethyleneimine [27]. Taken as whole, this perspective illustrates the broad practical value of molecular doping

and highlights the need for basic interface characterization such as we report.

Conclusion

To summarize, we have monitored and analyzed the doping effect of TCNQ adsorbates that partly compensate defects in bulk MoS₂. These surface studies complement earlier published work showing the effects of TCNQ on the optical properties of MoS₂ [3] by showing the effects of TCNQ on the electronic structure of MoS₂. The stepwise surface doping of bulk MoS₂ with TCNQ leads to a uniform shift of the band structure with respect to the Fermi level, which saturates at 0.2 eV. The shift arises due to charge transfer of excess electrons from the MoS₂ substrate to the acceptor molecule, which we directly observe through the presence of the former LUMO of TCNQ in the photoemission spectrum. Since there are no hybrid states, nor is there measurable distortion to the MoS₂ bands, our results indicate a direct charge transfer to the molecules on the surface. Given the known trion suppression of TCNQ, and from our comparison of the magnitude of the shift with the band gap of bulk MoS₂, we deduce that moving the Fermi level to mid-gap is not necessary for achieving significant improvements to the photoluminescent properties. However, we expect that a mid-gap Fermi level can be achieved using a surface dopant molecule with a higher electron affinity such as F₄-TCNQ.

It is important that the charge transfer interactions between the molecule and substrate do not lead to distortions of the substrate band structure and only a rigid band shift. It is very desirable to maintain the MoS₂ band structure details without perturbation from the doping. The capability to establish rigid band shifts emphasizes that molecular surface doping can be a viable strategy for controlling electronic structure in the full range of 2D materials using a variety of molecular adsorbates. In fact, molecular acceptors have been used to control the Fermi level position in graphene [28,29] and topological insulators [30,31] to great effect in compensating for unintentional n-doping. More recently, molecular acceptors and donors have been used to control the charge density in ultrathin (1-2 layer) FeSe superconductors [32]. Taken together, these results and our new interface studies of MoS₂ presented here show that molecular adsorbates are an important tool for controlling functionality and electronic structure in 2D materials.

Acknowledgements

This work was supported by the Army Research Office under contract W911NF-04-D-0003 and instrumentation support was provided by a UNC-GA-ROI grant.

References

- [1] K.S. Novoselov, A. Mishchenko, A. Carvalho, A.H. Castro Neto, 2D materials and van der Waals heterostructures, *Science* (2016) 353.
- [2] W. Chen, Q. Dongchen, X. Gao, A. Wee, Surface transfer doping of semiconductors, *Prog. Surf. Sci* 84 (2009) 279–321.
- [3] S. Mouri, Y. Miyauchi, K. Matsuda, Tunable photoluminescence of monolayer MoS₂ via chemical doping, *Nano Lett* 13 (2013) 5944–5948.
- [4] S. Tongay, J. Zhou, C. Ataca, J. Liu, J.S. Kang, T. Matthews, L. You, J. Li, J. Grossman, J. Wu, Broad-range modulation of light emission in two-dimensional semiconductors by molecular physisorption gating, *Nano Lett* 13 (2013) 2831–2836.
- [5] K.P. Dhakal, D.L. Duong, J. Lee, H. Nam, M. Kim, M. Kan, Y.H. Lee, J. Kim, Confocal absorption spectral imaging of MoS₂: optical transitions depending on the atomic thickness of intrinsic and chemically doped MoS₂, *Nanoscale* 6 (2014) 13028–13035.
- [6] S. Mouri, Y. Miyauchi, K. Matsuda, Chemical doping modulation of nonlinear photoluminescence properties in monolayer MoS₂, *Appl. Phys. Express.* 9 (2016) 055202.
- [7] K.F. Mak, K. He, C. Lee, G.H. Lee, J. Hone, T.F. Heinz, J. Shan, Tightly bound trions in monolayer MoS₂, *Nat Mater* 12 (2013) 207–211.
- [8] C.H. Lui, A.J. Frenzel, D.V. Pilon, Y.-H. Lee, X. Ling, G.M. Akselrod, J. Kong, N. Gedik, Trion-induced negative photoconductivity in monolayer MoS₂, *Phys Rev Lett* 113 (2014) 166801.

- [9] W. Zhou, X. Zou, S. Najmaei, Z. Liu, Y. Shi, J. Kong, J. Lou, P.M. Ajayan, B.I. Yakobson, J.-C. Idrobo, Intrinsic structural defects in monolayer molybdenum disulfide, *Nano Lett* 13 (2013) 2615–2622.
- [10] Y. Cai, H. Zhou, G. Zhang, Y.-W. Zhang, Modulating carrier density and transport properties of MoS₂ by organic molecular doping and defect engineering, *Chem. Mater.* 28 (2016) 8611–8621.
- [11] J.K. Ellis, M.J. Lucero, G.E. Scuseria, The indirect to direct band gap transition in multilayered MoS₂ as predicted by screened hybrid density functional theory, *Appl. Phys. Lett.* 99 (2011) 261908.
- [12] M. Gehlmann, I. Aguilera, G. Bihlmayer, E. Młyńczak, M. Eschbach, S. Döring, P. Gospodarič, S. Cramm, B. Kardynał, L. Plucinski, S. Blügel, C.M. Schneider, Quasi 2D electronic states with high spin-polarization in centrosymmetric MoS₂ bulk crystals, *Sci. Rep.* 6 (2016) 26197.
- [13] R. Suzuki, M. Sakano, Y.J. Zhang, R. Akashi, D. Morikawa, A. Harasawa, K. Yaji, K. Kuroda, K. Miyamoto, T. Okuda, K. Ishizaka, R. Arita, Y. Iwasa, Valley-dependent spin polarization in bulk MoS₂ with broken inversion symmetry, *Nat Nano* 9 (2014) 611–617.
- [14] S.W. Han, G.-B. Cha, E. Frantzeskakis, I. Razado-Colambo, J. Avila, Y.S. Park, D. Kim, J. Hwang, J.S. Kang, S. Ryu, W.S. Yun, S.C. Hong, M.C. Asensio, Band-gap expansion in the surface-localized electronic structure of MoS₂ (0002), *Phys Rev B* 86 (2012) 115105.
- [15] K.F. Mak, C. Lee, J. Hone, J. Shan, T.F. Heinz, Atomically thin MoS₂: A new direct-gap semiconductor, *Phys Rev Lett* 105 (2010) 136805.
- [16] K. Kam, B. Parkinson, Detailed photocurrent spectroscopy of the semiconducting group VI transition metal dichalcogenides, *J. Phys. Chem* 86 (1982) 463–467.
- [17] W. Jin, P.-C. Yeh, N. Zaki, D. Zhang, J.T. Sadowski, A. Al-Mahboob, A.M. van der Zande, D.A. Chenet, J.I. Dadap, I.P. Herman, P. Sutter, J. Hone, R.M. Osgood, Direct measurement of the thickness-dependent electronic band structure of MoS₂ using angle-resolved photoemission spectroscopy, *Phys Rev Lett* 111 (2013) 106801.
- [18] H. Peelaers, C.G. Van de Walle, Effects of strain on band structure and effective masses in MoS₂, *Phys Rev B* 86 (2012) 241401.
- [19] Y. Jing, X. Tan, Z. Zhou, P. Shen, Tuning electronic and optical properties of MoS₂ monolayer via molecular charge transfer, *J Mater Chem A* 2 (2014) 16892–16897.
- [20] R. Precht, R. Hausbrand, W. Jaegermann, Electronic structure and electrode properties of tetracyanoquinodimethane (TCNQ): a surface science investigation of lithium intercalation into TCNQ, *Phys Chem Chem Phys* 17 (2015) 6588–6596.
- [21] S.F. Lin, W.E. Spicer, B.H. Schechtman, Electron escape depth, surface composition, and charge transfer in tetrathiafulvalene tetracyanoquinodimethane (TTF-TCNQ) and related compounds: Photoemission studies, *Phys Rev B* 12 (1975) 4184–4199.
- [22] S. Das, H.-Y. Chen, A.V. Penumatcha, J. Appenzeller, High performance multilayer MoS₂ transistors with scandium contacts, *Nano Lett* 13 (2012) 100–105.
- [23] M.P. Seah, W.A. Dench, Quantitative electron spectroscopy of surfaces: A standard data base for electron inelastic mean free paths in solids, *Surf. Interface Anal.* 1 (1979) 2–11.
- [24] H. Qiu, T. Xu, Z. Wang, W. Ren, H. Nan, Z. Ni, Q. Chen, S. Yuan, F. Miao, F. Song, G. Long, Y. Shi, L. Sun, J. Wang, X. Wang, Hopping transport through defect-induced localized states in molybdenum disulphide, *Nat Commun* (2013).
- [25] D. Stradi, B. Borca, S. Barja, M. Garnica, C. Diaz, J.M. Rodriguez-Garcia, M. Alcami, A.L. Vazquez de Parga, R. Miranda, F. Martin, Understanding the self-assembly of TCNQ on Cu(111): a combined study based on scanning tunneling microscopy experiments and density functional theory simulations, *RSC Adv* 6 (2016) 15071–15079.
- [26] E.P. Nguyen, Excitation dependent bidirectional electron transfer in phthalocyanine-functionalised MoS₂ nanosheets, 8 (2016) 16276–16283.
- [27] Y. Du, H. Liu, A.T. Neal, M. Si, D.Y. Peide, Molecular doping of multilayer MoS₂ field-effect transistors: Reduction in sheet and contact resistances, *IEEE* 34 (2013) 1328–1330.
- [28] W. Chen, S. Chen, D. Chen Qi, X.Y. Gao, A.T.S. Wee, Surface transfer p-type doping of epitaxial graphene, *JACS* 129 (2007) 10418–10422.
- [29] C. Coletti, C. Riedl, D.S. Lee, B. Krauss, L. Patthey, K. von Klitzing, J.H. Smet, U. Starke, Charge neutrality and band-gap tuning of epitaxial graphene on SiC by molecular doping, *Phys Rev B* 81 (2010) 235401.
- [30] J. Wang, A.S. Hewitt, R. Kumar, J. Boltersdorf, T. Guan, F. Hunte, P.A. Maggard, J.E. Brom, J.M. Redwing, D.B. Dougherty, Molecular Doping Control at a Topological Insulator Surface: F₄-TCNQ on Bi₂Se₃, *J. Phys. Chem. C* 118 (2014) 14860–14865.
- [31] D. Kim, S. Cho, N.P. Butch, P. Syers, K. Kirshenbaum, S. Adam, J. Paglione, M.S. Fuhrer, Surface conduction of topological Dirac electrons in bulk insulating Bi₂Se₃, *Nat Phys* 8 (2012) 459–463.
- [32] J. Guan, J. Liu, B. Liu, X. Huang, Q. Zhu, X. Zhu, J. Sun, S. Meng, W. Wang, J. Guo, Superconducting transition of FeSeSrTiO₃ induced by adsorption of semiconducting organic molecules, *Phys Rev B* 95 (2017) 205405.