2D Materials

PAPER

The squeezable nanojunction as a tunable light-matter interface for studying photoluminescence of 2D materials

Matthias A Popp, Malte Kohring, Alexander D Fuchs, Sascha Korn, Narine Moses Badlyan, Janina Maultzsch and Heiko B Weber

Department of Physics, Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Erlangen D-91058, Germany
* Author to whom any correspondence should be addressed.
E-mail: heiko.weber@fau.de

Keywords: molybdenum disulfide, optical coupling, photoluminescence, squeezable nanojunction

Abstract

We study photoluminescence (PL) of MoS$_2$ monolayers in optical cavities that can be tuned in operando. Technically, we use the recently developed squeezable nanojunction (SNJ). It is a versatile mechanical setup that has been useful to study thermoelectric effects at electronic tunneling distances. Here, we emphasize on a cavity with 0–3 micrometer distance with optical access. Due to the tunable cavity, we see strong distortions of PL spectra. By an analysis of the ensemble, we identify a normalization protocol that gives access to disentangling the contributions from excitation, gating and emission. The systematic evolution of data reconfirms the drastic influence of the local electromagnetic mode budget on the spectral properties. The experiment further underscores the broadband application range of the SNJ technique, able for combining (nano-) electronic functionality with optical access and a tunable light-matter interface.

1. Introduction

The scanning tunneling microscope (STM) with its atomic resolution and picometer distance control has revolutionized nanoscience. For the investigation of two-dimensional (2D) layered materials, an analogue technique would be desirable which provides picometer distance control, and—different to STM—unobscured optical access. The squeezable nanojunction (SNJ) technique provides many of these properties (it does, however without lateral atomic control). After a first appearance decades ago [1–5], it has recently been rediscovered for studying thermoelectric effects in single-molecule-like contacts [6, 7]. Figure 1(a) displays a schematic of the SNJ: two chips (silicon carbide or fused silica) are mounted face to face with a spacer that impedes initial contact. By pressing via a spring from underneath, the distance of the chip surfaces can be fine controlled. This setup is ultrastable and transparent [6, 7]. Dif-ferent to our previous experiments we add a scanning confocal microscope for optical microscopy and spectroscopy. As a 2D luminescent sample, we place a monolayer MoS$_2$ flake on the surface of the upper chip; the lower chip is chosen to be either a mirror (see figures 1(b) and (c)) or a transparent dielectric.

Nearly any optical investigation of 2D materials includes an electromagnetic environment. Often, SiO$_2$ on silicon, fused silica or similar dielectrics are used as substrates. Any of such stacks brings in (multiple) reflections, which provide built-in Fabry–Perot (F–P)-like phenomena. The importance of the associated patterns of the electromagnetic field in which the 2D material is located has been recognized [8–10]. The method we present is suited to explore the interaction between a continuously varied F–P stack and the 2D material systematically on the very same sample spot. We see strongly distorted spectra and trace their evolution. The data raise awareness of potential artifacts and allow for a refined insight of PL in 2D materials.

2. Photoluminescence of MoS$_2$ in a dielectric Fabry–Perot stack

In this section, we discuss the situation of two parallel dielectric plates, with a MoS$_2$ monolayer being
attached to the upper chip (figure 2(a)). Fully reflecting mirrors are absent in this section. A first experimental necessity is the determination of the distance \( d \) between the two plates. For this purpose, we use essentially white-light interferometry within the same optical setup.

The calibration curve thus obtained is displayed in figure 2(b) with nanometer resolution, see SI (available online at stacks.iop.org/2DM/8/045034/mmedia). From here on, we present all data as a function of \( d \). Figure 2(c) shows regular F–P lines which have a common origin at \( d = 0 \).

We now face to the PL measurement of the MoS\(_2\) flake (figure 2(d)). For excitation, we use a green laser (\( \lambda_{\text{laser}} = 532 \) nm). The well-known spectral feature at 680 nm, which is composed of the A exciton and the A\(^-\) trion [11–14] is dominant. In this experiment, we emphasize on its distance dependence, which is only on a first glance periodic in \( d \). Our setup allows, however, for a more detailed view on the interaction of the flake’s optical response with the given electromagnetic environment. In this representation, one can identify variations in peak position (on the 10 nm scale), peak height and peak width. Altogether, the geometry introduces a significant distortion of the spectral features. Our extensive data set allows for further decomposition of the contributing effects. Normally, one is interested in the spectral features of the flake and considers the electromagnetic environment as a weak perturbation. Here, we study in detail the deviations caused by the environment. For this purpose, we divide the data by a distance-averaged spectrum. This leads to figure 2(e), where the enhancement/suppression factor is singled out. One can identify a regular pattern of peaks, the positions of which are located on horizontal and tilted lines.

We first address the horizontal lines, which appear equidistant in \( d \). Their origin is the well-defined intensity variation of the excitation field. By tuning \( d \), the interference conditions in the F–P stack are altered. As a result, the excitation field intensity is oscillatory in \( d \) with a periodicity of \( \lambda_{\text{laser}}/2 \). In linear approximation, this affects the entire emission spectrum equally. If this was the only effect, we would expect only vertical periodicity, but not the obvious variations of spectral weight within the horizontal lines in figure 2(e).

The F–P stack, however, influences also the emission coupling strength. As the PL feature of MoS\(_2\) has a significant spectral width, it inherits in parts the tilted lines of the white-light spectrum (cf. figure 2(c)). The result is a wavelength-dependent coupling function, which is now oscillatory in \( \lambda \) and \( d \). We can separate it from the data by again normalizing the data set, now along the \( \lambda \)-axis (at least for those data where every horizontal line includes sufficient \( \lambda \)-averaging). This procedure approximately averages out the influence of the excitation. The result is displayed in figure 2(f): we find indeed the diagonal lines that are reminiscent of the white-light data (cf. figure 2(c)).

Hence, when light matter coupling is simultaneously strong both for excitation and emission, i.e. at
Figure 2. (a) Scheme of the material stack underlying this panel. (b) Calibration curve of Piezo voltage vs distance retrieved from white light interferometry. (c) Normalized reflectance data (white light interferometry). (d) PL spectra. Upon variation of the geometry, the excitonic peak is warped by F–P effects. The distance-averaged spectrum $\langle PL \rangle_d$ is drawn as a red line. (e) After normalization of the PL data from (d), the coupling factor $c$ due to F–P is extracted. (f) Subsequent to the latter normalization, a second normalization compensates the F–P modulation of the excitation. Data at $\lambda < 600$ nm are affected by artifacts due to the uncompensated influence of Raman features of the SiC substrate. (g) Coupling factor simulated within a transfer matrix model for normal incidence. (h) Coupling factor simulated for incidence angles up to 22° with respect to the surface normal, with excellent agreement to the experimental data of (e).

3. Photoluminescence of MoS$_2$ in front of a mirror

Conceptually, the experiment is simplified when replacing one dielectric chip by a mirror (see figure 3(a)). Then, the physics essentially boils down to a 1D textbook picture of standing electromagnetic waves in front of a mirror (cf. figures 1(b) and (c)). The SNJ technique with its high spatial accuracy is able to move a MoS$_2$ flake continuously within the standing wave pattern. In particular, we can address the spatial region of the first and second node/antinode in front of the mirror. Obviously, the different wavelengths involved (excitation at 532 nm, PL signature from 600 to 800 nm) etc will have nodes at different positions, which is graphically displayed in figures 1(b) and (c). The sample flake can be moved through this pattern. In a distance range of 0–700 nm, the respective nodes are well ordered and separated. The electromagnetic environment induces strong spectral distortions to the PL spectra, both in intensity and shape. Figure 1(d) displays the crossing of horizontal and diagonal lines, a peak results in figure 2(e). Note that the data in figures 2(e) and (f) are purely based on experiments, only their interpretation relies on the F–P model. For comparison, we performed transfer-matrix method simulations [15], which compute the light-matter enhancement factor, but not the spectral properties of the sample flake. The result is displayed in figure 2(g) for normal incidence, which reproduces qualitatively the experimental data analysis of figure 2(e), however with subtle deviations in peak shape, intensity and position. The agreement between experiment and simulation is more accurate when, in addition, finite emission angles are included ($\theta_{\text{max}} = 22^\circ$ for best fit to data, see figure 2(h), corresponding to an effective numerical aperture of NA = 0.37, which is slightly below the objective characterization of NA = 0.42). Main deviations occur at the left side of the presented spectra, because there, the signal is weak due to its suppression by the dichroic mirror.

In this regime of weak quality factors, we can approximately consider the excitation, the internal effects in the MoS$_2$ flake and the emission as separated phenomena. This can be mapped on a model where the corresponding rates factorize. As a consequence, we could successfully implement a protocol that separates the spectral properties of the flake and the spectral distortions of the electromagnetic (F–P) environment reliably without involving further model assumptions. When the quality factor of the resonators is further enhanced, we expect a more complex interplay of coupling strength and internal processes of MoS$_2$ [16].
negative ($d \approx -20\,\text{nm}$) which is due to the reflection phase at the gold mirror surface. Also, the slope of the tilted lines deviates slightly from $n\lambda/2$ due to inclusion of emission angles $\neq 0^\circ$ to the surface normal ($NA > 0$). We conclude that the MoS$_2$ PL feature with its significant spectral width experiences strong deformation by the electromagnetic environment. While the effect itself is not unknown, the experiments with the SNJ technique can quasi-continuously vary the electromagnetic environment and thus make the drastic influence of both excitation and emission mode structure accessible.

4. Photoluminescence of gated MoS$_2$ in an optical cavity

In many previous PL experiments, the influence of electrostatic gating on exciton/trion formation etc has been investigated thoroughly (within a static F-P stack) [11, 12]. In the previous sections, we have demonstrated the strong impact of the tunable electromagnetic mode pattern. It is desirable to combine both parametric variations within a single experiment. For this purpose, we have defined a two-mirror cavity (cf. figure 4(a)). One mirror is a 50 nm gold layer on the bottom chip, the other is a partially transparent Al layer (5 nm thickness) on the upper chip, which is then overcoated with a transparent sputtered SiO$_2$ dielectric. The MoS$_2$ monolayer is deposited on the latter, such that approximately $\lambda/4$ conditions are met for the emission wavelength. The flake is electrically contacted by a gold electrode from the side. In contrast to the previous section with a single mirror, the second metal sheet not only provides an optical cavity with enhanced quality factor, it simultaneously allows to control the charge density within the flake independently via a gate voltage $V_G$ applied between the Al gate and the flake. Figures 4(b) and (c) display the PL spectra for a gate voltage $V_G = 0\,\text{V}$ (b) and $V_G = -16\,\text{V}$, respectively. The overall shape of both patterns is similar. The main difference appears in intensity; further subtle differences in peak shape can be recognized. The optical coupling factor (figure 4(d)) is determined in full analogy to figure 2(e), i.e. by normalizing with an ensemble-averaged spectrum. A comparison to the previous single-mirror case shows two main differences: (a) the peak features are sharpened due to the improved cavity and (b) the peak features are asymmetric due to the asymmetric placement of the MoS$_2$ flake in the cavity.

We contrast this analysis with another that is intended to remove the influence of the coupling factor and takes into account mainly the electrical response; figure 4(e) plots the ‘gateability’ $g$, which we define as:

$$g = \frac{\text{PL}(V_G = -16\,\text{V}, \lambda, d)}{\text{PL}(V_G = 0\,\text{V}, \lambda, d)}$$
i.e. the data plotted in figure 4(c) divided by those in figure 4(b). On the first sight, one may expect that the influence of the optical cavity should be cancelled by this normalization resulting in d-independent behavior of $g$ (which would be the case if the MoS$_2$ PL quantum efficiency would be only a function of $\lambda$ and $V_G$). The peak feature at 660 nm arises because of the (uncharged) exciton and (charged) trion statistics are differently affected by the electrochemical potential $[12]$: if free electrons are present, excitons will combine with electrons and thus form trions, the latter of which decay mainly nonradiatively. Therefore, by applying a negative gate voltage, free electrons are removed from the MoS$_2$ and exciton PL features are enhanced.

The clear $d$-dependent patterns in figure 4(e) reveal, however, an interplay between optical and electrical parametrization. This modulation is periodic with half the excitation laser wavelength. We attribute this main effect to the dependence of the gateability on excitation intensity/generation rate (i.e. the quantum efficiency is also a function of the excitation amplitude $[12]$.). Its modulation with $d$ stems from the modulation of the laser intensity at the flake’s position (with a period of $\lambda_{laser}/2$). Remote from the peak region, a remaining modulation with $d$ and $\lambda$ can be observed, reminiscent of the diagonal lines of the coupling factor (figure 4(d)). One may argue that these lines stem from wavelength-dependent variations of the radiative decay times of both excitons and trions $[17]$, which interact with their gate-dependent decay statistics. However, the weak signals remote from the peak can also be affected by incomplete background subtraction so that artifacts cannot reliably be excluded. More information may be gained with time-resolved PL measurements $[17–19]$. Overall, the nontrivial structure of the gateability underscores that the mode structure of the cavity is required to understand the gate response of PL in detail.

5. Conclusions and outlook

We have presented PL measurements of a monolayer MoS$_2$ flake. Due to a continuous variation of the electromagnetic environment/cavity, the interplay of the latter with PL becomes particularly clear. We observe variations of the PL intensity, which reach the order of 100 in our experiments but are theoretically not limited. Variations of the excitation mode at the position of the 2D-material cause predominantly intensity variations, whereas variations of the (wavelength dependent) emission modes may strongly shift or distort the spectral features. This is certainly more than a playful variation of artifacts: our experiments elucidate the strong impact of a purely dielectric F–P stack or, even more drastically, the impact of reflecting surfaces. Both are omnipresent in PL investigations of 2D materials. Finally, we have demonstrated experimentally that the interplay of electrostatic gating and geometry variations is not trivial. The method used, the SNJ, has proven to be valuable for optical investigations of 2D materials. Because it operates with a small mode volume, it can be further optimized towards the strong coupling regime $[16, 20]$.

6. Methods

MoS$_2$ preparation: The MoS$_2$ flakes were prepared by mechanical exfoliation from a bulk MoS$_2$ crystal using bluetape. After mechanical exfoliation the thin MoS$_2$ flakes were transferred on polydimethylsiloxane film ($5 \times 5$ mm$^2$). Monolayer (1L) MoS$_2$ flakes were identified by optical contrast and PL measurements. Then an individual 1L MoS$_2$ flake was transferred onto a chip using all-dry transfer method $[21]$. Finally, the successful transfer of the 1L MoS$_2$ flake onto the SiC chip was confirmed by PL measurements.

SNJ, chip preparation: $8 \times 4$ mm chips were cut from semi-insulating 4H-SiC wafer material and cleaned wet-chemically by a standard RCA procedure. By means of optical lithography and CF$_4$ plasma-etching 1 $\mu$m of the surface was removed, excluding mechanical contact points and sockets on which MoS$_2$ was subsequently placed (this helps to keep surface impurities from preventing the touching regime.). Electrical leads were fabricated by means of optical lithography and sputtering (Al, SiO$_2$) or e-beam evaporation (Au).

SNJ, mechanical setup: Chip holders including micrometer screws for lateral positioning of the two
chips were used, allowing for lateral relative positioning accuracy of few μm. The bending force is exerted on the bottom chip via a mandrel that is tensioned via a piezo-spring-lever mechanism. The spring is pre-tensioned with a motorized screw to allow for a larger range. Mechanical parts are mounted into a Cryo-Vac vacuum vessel. The whole mechanical setup can be scanned inside the vacuum vessel with a motorized x–y stage. Measurements of figures 1–3 were performed under vacuum conditions and measurements of figure 4 under ambient conditions. All experiments were carried out at room temperature. A closer technical description is given in SI.

Optical setup: A custom-built confocal microscope with excitation capabilities including a 532 nm continuous wave laser and tungsten incandescent light (for orientation and white light interferometry) was used. Excitation light is directed to the sample via a dichroic mirror and focused via a LCPLFLN20xLCD Olympus objective specified with NA = 0.42, and characterized NA = 0.42. Laser spot sizes were on the order of 2 – 3 μm and therefore all measured properties restricted to this area (for white light interferometry due to pinhole). The variation of d within the focus area is orders of magnitude smaller than the wavelength, see SI. PL and reflected light is collected with the same objective, passes the dichroic mirror and is filtered with a long pass filter before detection. An Andor Shamrock 500i Spectrometer with Andor Newton 920 camera were used for spectroscopy. Motorized flip mounts were used for fully automated switching between light sources as well as between imaging and spectroscopy mode, allowing for over-night measurements.

Transfer matrix method (TMM) calculations: As a starting point we used the python TMM package [15]. Drastic numerical speed-up could be achieved by using the following steps: (a) directly substitute all fixed parameters with numerical values. (b) Evaluate transfer matrix multiplications symbolically using the SymPy package [22]. (c) Create numpy [23] functions (using numpy.frompyfunc). (d) Evaluate functions for all desired parameter combinations.

Normalization of reflectance spectra and distance calibration: Reflectance spectra were recorded at the same spot as PL spectra but with tungsten lamp illumination. Normalized reflectance spectra for distance calibration were produced with the following routine: (a) reflectance spectra for a wide range of (unknown) plate distances were recorded (by sweeping the piezo voltage V\text{Piezo}). (b) Averaging for every λ along V\text{Piezo} over an integer number of oscillations to remove d-dependence, yielding a calibration spectrum. (c) Division of all (d-dependent) raw spectra by calibration spectrum. Finally, d was calculated by parameter optimization to the reflectivity within a TMM model of the material stack under investigation.

Simulation of coupling factors: Coupling factors were calculated as c = c_{\text{exc}} × c_{\text{emit}} with the excitation coupling factor c_{\text{exc}} = c_{\text{mmn}}(\lambda_{\text{laser}}, d) and the emission coupling factor c_{\text{emit}} = c_{\text{mmn}}(\lambda, d). Herein, c_{\text{mmn}}(\lambda, d) is the fraction of light intensity of incident light of wavelength λ with respect to the intensity at the position of MoS_2 gained with a TMM model of the material stack under investigation. For inclusion of finite emission angles θ, angle-dependent emission coupling factors c_{\text{mmn}}(\lambda, d, θ) were calculated and averaged over θ after weighting by sin(θ).

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft (DFG), Projektnummer 182849149 (SFB 953, projects B08 and B13). We acknowledge useful discussions with S Götzinger.

Supporting information

The supporting information enclose a detailed technical description of our SNJ setup with optical access, as well as an analysis of distance variation within the focus spot.

ORCID iDs

Matthias A Popp  https://orcid.org/0000-0001-7620-1245
Malte Kohring  https://orcid.org/0000-0002-3344-9133
Alexander D Fuchs  https://orcid.org/0000-0003-1896-9242
Sascha Korn  https://orcid.org/0000-0003-4340-5163
Narine Moses Badlyan  https://orcid.org/0000-0003-0992-6507
Janina Maulitzsch  https://orcid.org/0000-0002-6088-2442
Heiko B Weber  https://orcid.org/0000-0002-6403-9022

References

[1] Moreland J, Alexander S, Cox M, Sonnenfeld R and Hansma P K 1983 Squeezable electron tunneling junctions Appl. Phys. Lett. 43 387–8
[2] Moreland J and Hansma P K 1984 Electromagnetic squeezer for compressing squeezable electron tunneling junctions Rev. Sci. Instrum. 55 399–403
[3] Hansma P K 1986 Squeezable tunneling junctions IBM J. Res. Dev. 30 370–3
[4] Vadai M, Nachman N, Ben-Zion M, Bürkle M, Pauly F, Cuevas J C and Selzer Y 2013 Plasmon-induced conductance enhancement in single-molecule junctions J. Phys. Chem. Lett. 4 2811–6
[5] Vadai M and Selzer Y 2016 Plasmon-induced hot carriers transport in metallic ballistic junctions J. Phys. Chem. C 120 21063–8
[6] Popp M A and Weber H B 2019 An ultra-stable setup for measuring electrical and thermoelectrical properties of nanojunctions Appl. Phys. Lett. 115 083108
[7] Popp M A, Erpenbeck A and Weber H B 2021 Thermoelectricity of near-resonant tunnel junctions and their relation to Carnot efficiency Sci. Rep. 11 2031
[8] Lien D-H et al 2013 Engineering light outcoupling in 2D materials Nano Lett. 15 1556–61
[9] Riedel D, Sollner I, Shields B J, Starosielec S, Appel P, Neu E, Makhtinsky P and Warburton R J 2017 Deterministic enhancement of coherent photon generation from a nitrogen-vacancy center in ultrapure diamond Phys. Rev. X 7 031040
[10] Schwarz S et al 2014 Two-dimensional metal-chalcogenide films in tunable optical microcavities Nano Lett. 14 7003–8
[11] Mak K F, He K, Lee C, Lee G H, Hone J, Heinz T F and Shan J 2013 Tightly bound triions in monolayer MoS2 Nat. Mater. 12 207–11
[12] Lien D-H, Uddin S Z, Yeh M, Amani M, Kim H, Ager J W, Yablonovitch E and Jayvee A 2019 Electrical suppression of all nonradiative recombination pathways in monolayer semiconductors Science 364 668–71
[13] Schueschner N, Ochędowski O, Kaulitz A-M, Gillen R, Schleberger M and Maultzsch J 2014 Photoluminescence of freestanding single- and few-layer MoS2 Phys. Rev. B 89 125406
[14] Wang G, Chernikov A, Glazov M M, Heinz T F, Marie X, Amand T and Urbaszek B 2018 Colloquium: excitons in atomically thin transition metal dichalcogenides Rev. Mod. Phys. 90 021001
[15] Byrnes S J 2016 Multilayer optical calculations (arXiv:1603.02720 [physics.comp-ph])
[16] Flatten L C, He Z, Coles D M, Trichet A A P, Powell A W, Taylor R A, Warner J H and Smith J M 2016 Room-temperature exciton-polaritons with two-dimensional WS2 Sci. Rep. 6 1–7
[17] Fang H H et al 2019 Control of the exciton radiative lifetime in van der Waals heterostructures Phys. Rev. Lett. 123 067401
[18] Chizhik A I, Chizhik A M, Khoptyar D, Bør S, Meixner A J and Enderlein J 2011 Probing the radiative transition of single molecules with a tunable microresonator Nano Lett. 11 2700–3
[19] Robert C et al 2016 Exciton radiative lifetime in transition metal dichalcogenide monolayers Phys. Rev. B 93 205423
[20] Junginger A, Wackenhut F, Stuhl A, Blendinger F, Brecht M and Meixner A J 2020 Tunable strong coupling of two adjacent optical λ/2 Fabry-Pérot microresonators Opt. Express 28 485
[21] Castellanos-Gomez A, Buscema M, Molenar R, Singh V, Janssen L, van der Zant H S J and Steele G A 2014 Deterministic transfer of two-dimensional materials by all-dry viscoelastic stamping 2D Mater. J 011002
[22] Meurer A et al 2017 SymPy: symbolic computing in python PeerJ Comput. Sci. 2017 e103
[23] Harris C R et al 2020 Array programming with NumPy Nature 585 357–62