Iris Niehues

Strain-controlling the optical properties of 2D semiconductors on the micro- to nanoscale

Two-dimensional (2D) materials consist of only a very small number of atomic layers or molecules and therefore most of the physics happens only in two dimensions. Among the big variety of 2D materials, half-metallic graphene (one single atomic layer of graphite) and 2D semiconductors are of particular interest. They became a prominent subject of fundamental research in the last years as well as in applications for flexible displays and solar panels. The unique properties of graphene [1] and atomically thin semiconductors [2-5] were already theoretically predicted as early as the 1940s and further discussed through the 1980s. Nevertheless, it took decades until the fabrication of 2D materials was realized in experiments for the first time. The reason was, among others, the assumption that such materials could not exist, because Peierls and Landau had calculated in the 1930s [6, 7] that crystals in one or two dimensions are thermodynamically unstable. It did therefore take until 2004 for graphene to be purposefully prepared. Its stability was demonstrated for the first time by Konstantin S. Novoselov and Andre K. Geim [8, 9]. Both physicists were awarded the 2010 Nobel Prize in physics for their achievements. Quickly, the adhesive tape method - used to produce graphene - was applied to other layered materials, such as hexagonal boron nitride (hBN) and transition metal dichalcogenides (TMDCs) [10]. Their 3D host crystals have weak van der Waals bonding between the layers, whereas the atoms within one layer have significantly stronger covalent bonds. This is the reason why individual layers can be easily separated from the bulk crystal by mechanical cleavage, e.g., using the adhesive tape method. Figure 1 (a) and (b) illustrate the crystal structure and the mechanical exfoliation process of a TMDC crystal. A single TMDC layer (monolayer) consists of three layers of atoms as the smallest building block. In the ball and stick scheme the atoms are shown as blue and yellow balls and the covalent bonds as black sticks. A typical TMDC bulk crystal is shown in Fig. 1 (b) (top). By using an adhesive tape, the van der Waals bonds between the individual layers can be broken, such that individual layers are removed from the bulk crystal (middle) which can then be transferred on a substrate of choice for further investigation (bottom). Afterwards, single layers can be identified under an optical microscope thanks to their optical contrast. Figure 1 (c) shows an optical micrograph of a mechanically exfoliated tungsten diselenide (WS_2) flake with different layer thicknesses - ranging from monolayer via bilayer to few-layer regions (left to right) - on a polymer substrate. Today, also liquid exfoliation methods are commonly used [11]. The reduction of the physical dimension has several important consequences which are highly dependent on the investigated material.

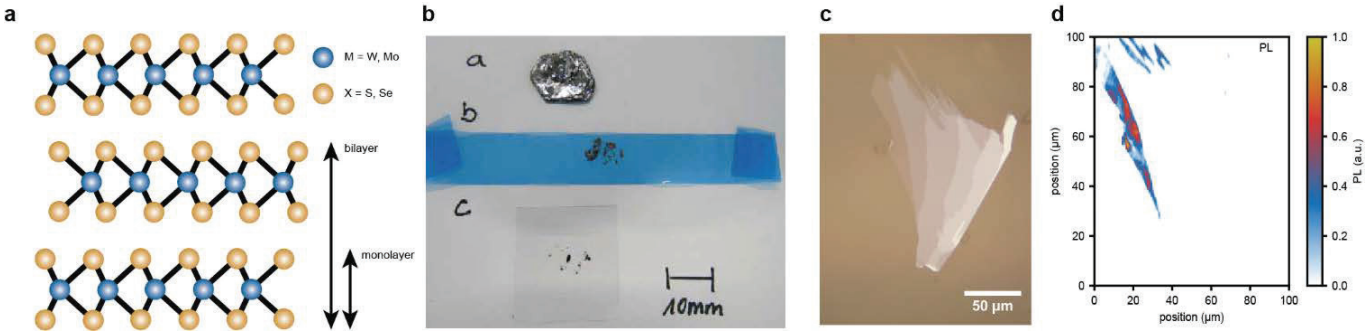

Fig. 1: Preparation and identification of 2D materials. (a) Crystal structure of a TMDC (ball and stick scheme). Atoms are shown as blue and yellow balls, strong covalent bonds are indicated by black sticks. (b) Mechanical exfoliation process. Top: bulk WS_2 crystal. Middle: WS_2 flakes on scotch tape. Bottom: final WS_2 sample on a polymer. (c) exfoliated WS_2 crystal in white-light reflection. Mono-, bi-, tri- and multilayers from left to right. (d) Photoluminescence image of the exfoliated flake shown in (c). Only the monolayer region shows a bright signal.

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Among the most intensely investigated layered materials are the TMDCs molybdenum disulfide (MoS_2), molybdenum diselenide ($MoSe_2$), tungsten disulfide (WS_2), and tungsten diselenide (WSe_2), which are semiconductors independent of their number of layers. However, they possess a direct optical band gap only in the form of a monolayer, while they are indirect

semiconductors already as a bilayer. This effect was first demonstrated in 2010 by Kin Fai Mak et al. [12] and Andrea Splendiani et al. [13] for a MoS_2 monolayer. Shortly after that, $MoSe_2$, WS_2, and WSe_2 monolayers have also been identified as direct band gap and hence "bright" semiconductors as well [14, 15]. All of these monolayer types exhibit a strong photoluminescence (PL), i.e., light emission, signal in the visible or near infrared spectral range and are thus of prime interest for opto-electronic and particularly for solid-state lighting applications. A PL image of the WS_2 monolayer in Fig. 1 (c) is shown in (d), where one can clearly see that only the elongated monolayer region of the crystal lights up in the image, proving its strong optical response. The optical properties of TMDCs are dominated by excitons, which are bound electron-hole pairs. To judge the optical quality of a material, the spectral line widths of its bright transitions are a common indicator. At room temperature, the line widths of the exciton resonances in TMDC monolayers are determined by the interaction with lattice vibrations (phonons). In addition, just like graphene [16, 17], TMDC monolayers are mechanically extremely flexible, yet at the same time robust and can withstand mechanical strain of up to 10% [18, 19]. However, as known from graphene, the material properties can be changed over large areas by stretching [20]. As the detailed properties of any crystal crucially depend on its lattice structure, uniaxial straining, which changes the lattice constant in one direction, affects the band structure and consequently the optical properties of the crystal [21]. Thus, the question arises to what extent the optical properties of the atomically thin semiconductors can be changed by stretching and if such opto-mechanical effects can be used to generate new functionalities.

Strain can also be applied locally to the thin layers and therefore only alter the optical properties at specific locations in the flake. In this context an important achievement was the creation of spatially localized excitons in TMDC monolayers with the help of strain engineering [22] as illustrated in Fig. 2 (a). These localized excitons were found to show single-photon emission, which is a key step towards quantum technological applications of these materials. Quantum computer concepts rely on the realization of qubits, i.e., two-level systems, which can be realized as single photons ("flying qubits") or as the quantum states of the emitters themselves.

Research on strained TMDCs

My work focusses on the influence of strain on the optical properties of atomically thin TMDC materials. I am aiming to get a basic understanding of the underlying fundamental physical processes governing the interplay between strain and optical properties. For this purpose, one can perform white-light absorption and PL measurements for different strain values. For the experiments, TMDC layers are first prepared from the bulk crystal via micromechanical thinning and their thickness is determined under a white-light reflectance microscope and by PL mapping (see Fig. 1 (b-d)). Subsequently, monolayers and bilayers are deposited onto a flexible polycarbonate substrate by a dry stamping process [23]. Strain can then easily be applied to the atomically thin crystals by bending the substrate as indicated in Fig. 2 (b). Placing the substrate between two translation stages and reducing their distance will bend the substrate up. This creates a tension on the upper surface (highlighted in the blue circle) where the thin layer is placed. Therefore, the TMDC crystal experiences stretching in one direction, i.e., uniaxial tensile strain. One can determine the amount of strain by measuring the deflection *d*, the distance between the substrate edges *L* and its thickness *h*. As mentioned before, the optical spectra of 2D semiconductors are dominated by exciton resonances, so that the influence of strain on exciton energies, line widths, and overall brightness can be investigated with white-light absorption and PL spectroscopy. We have shown that applying uniaxial strain to atomically thin semiconductors provides a simple way to control exciton resonances [24] (Fig. 2 (c)). When plotting the measured exciton resonance energy of a WSe_2 monolayer as a function of the applied strain (Fig. 2 (d)), one finds a linear dependence with a slope of -49 meV/%, which is the so-called calibration or gauge factor. We have systematically determined

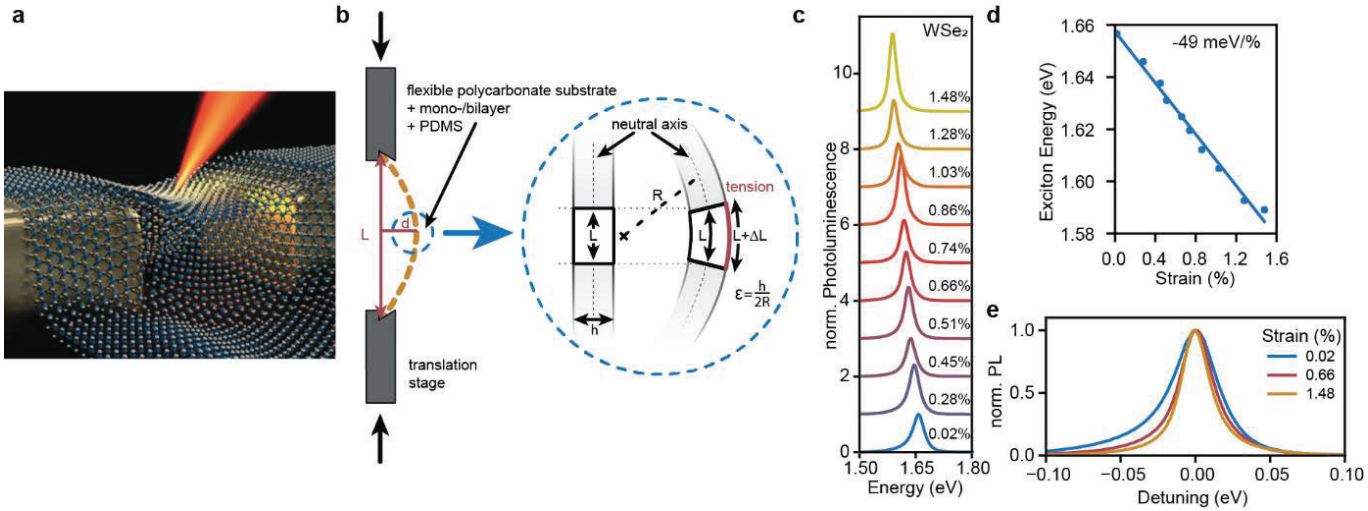

Fig. 2: Straining 2D materials. (a) Artistic illustration of a strain-induced single-photon emitter in a WSe_2 monolayer [22]. (b) schematics of a two-point bending apparatus. (c) Photoluminescence of a WSe_2 monolayer under strain (color coded from blue to yellow). (d) A exciton energy under strain extracted from (c) (dots) and linear fit. The gauge factor is -49 meV/%. (e) Line width of the A exciton under strain. With increasing strain (blue to yellow) the line becomes more symmetric and narrower [24].

these calibration factors for all four common TMDC materials MoS_2, $MoSe_2$, WS_2, and WSe_2 in mono- and bilayer form, both in absorption and PL spectra [24, 25]. The values are in good agreement with theoretical calculations. We also found that not only the exciton energy but also the exciton-phonon coupling is affected by strain, which manifests in a change of the spectral width of the exciton resonances (Fig. 2 (e)) [24, 25]. Thus, the application of strain offers the possibility to study and understand basic physical coupling mechanisms in 2D semiconductors in addition to the already mentioned realization of strain induced single-photon emitters.

In mechanically thinned TMDC bilayers, additional excitons appear in the optical spectra. While it became clear, that these resonances stem from excitons where electron and hole are distributed over both layers, the corresponding locations in the band structure were not entirely known. With the help of strain, it was possible to determine the energy shift of this so-called interlayer exciton in a MoS_2 bilayer and confirm that electron and hole are located at the K-point in the Brillouin zone, which is the same location as the normal intralayer excitons known from monolayers [26]. This result establishes strain-tuning experiments as useful tools to investigate optical transitions also in more complex multilayer structures, the so-called van der Waals heterostructures. Here, different layers of 2D materials are stacked vertically on top of each other, opening the possibility to create desired optical properties. The idea for this layered, atomistic material design dates back to Richard Feynman, who envisioned this modern development in his famous talk 'There's plenty of room at the bottom' in 1959.

In order to make real world applications, e.g., in the form of strain sensor layers based on TMDCs [27], high-quality crystals of macroscopic size are needed. While the mechanical exfoliation method using scotch tape is limited to the isolation of monolayers in the range of up to a few 100 micrometers, deterministically grown monolayers offer the possibility of centimeter-scale industrial production. However, in contrast to mechanically thinned samples, chemically grown TMDC monolayers have grain boundaries between the many differently oriented single crystals. The crystal orientation of the single grains and their boundaries can be visualized with optical techniques, which are polarization-dependent, e.g., frequency doubling (second harmonic generation, SHG). We were able to show that the deterministically applied strain is flawlessly transferred across grain boundaries and that the grown TMDC monolayers therefore exhibit similar opto-mechanical properties as mechanically thinned single-crystal layers [28]. They are thus suitable for use in strain sensors and other future opto-mechanical applications and technologies.

Conclusions

2D materials will revolutionize the future of flexible devices due to their outstanding optical and mechanical properties. The combination of monolayers and strain can create single-photon emitters which are the basis for future quantum technology applications. My work contributes to the fundamental understanding of the interplay between light, charge carriers, and lattice excitations in atomically thin semiconductors. It thus forms the basis to develop applications at the interface between photonics (application of light) and phononics (application of lattice vibrations). Future research on 2D materials will focus on the stacking of different materials (playing "Lego" with 2D materials). This will offer the possibility to design desired optical, electronic, magnetic properties, to name a few. In combination with strain one can imagine creating and manipulating desired optical properties, paving the way for the next generation of photonic quantum devices.

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ZITATBOX

Alfred Nobel (1833 - 1896)

„Man muss den Nächsten so behandeln, wie man von ihm behandelt sein will.“

„Ein Lexikon handhaben wissen, ist besser als zu glauben, ein solches zu sein.“

„Die Schwierigkeiten wachsen, je näher man ans Ziel kommt.“

„Wenn ich 1000 Ideen hätte und nur eine sich als gut erweisen würde, wäre ich zufrieden.“

Quelle: https://gutezitate.com/autor/alfred-nobel

Dr. Iris Niehues

Already in school I had a great interest in science and took part in a Jugend forscht competition. It was soon clear to me that I wanted to become a scientist. So, I decided to study physics after my Abitur.

I finished my masters at the University of Münster in 2015 focusing on solid state physics and optics. Already for my master thesis I investigated the optical properties of 2D materials and their manipulation on the nanoscale. I continued my research in this field during my PhD where I used mechanical strain to control optically active excitons (bound electron-hole pairs) and their interplay with phonons (lattice vibrations). Both my master and PhD thesis were supervised by Prof. Rudolf Bratschitsch and were awarded as the best thesis of the year in the physics department of the University of Münster.

Currently, I am working as a postdoctoral researcher with a DFG scholarship in the group of Prof. Rainer Hillenbrand at nanoGUNE, a research institute in San Sebastián, Spain. The research center combines world-class research on nanoscience and the comfort of a beautiful city and excellent food. In my project I am studying the optical properties of single-photon emitters (SPE) in hexagonal boron nitride (hBN) on the nanoscale. SPEs are a key building block for future optics-based quantum technology. With my research I want to develop a deeper understanding of the fundamental physics and contribute to the functionalization of these emitters in real world devices.