Single-Photon Emitters in Layered Van der Waals Materials

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Single-photon emitters (SPEs) have recently been discovered in various atomically thin materials. Their properties, controllability, and the possibility of their monolithic integration in electronic and photonic device structures make them attractive candidates for a wide range of applications in quantum information and communication, and also in other fields of physics and technology. In this review article, an overview of SPEs in layered van der Waals materials and their physical properties is given, theoretical concepts for the modeling of their level structure and their coupling to phonons are presented, and techniques for the creation and localization of these emitters in the host material are described. Perspectives for their application in various fields, such as their coupling to photonic resonators and waveguides, their control by external electric fields or strain, and their integration in optomechanical devices are discussed. Finally, functionalities relying on properties beyond single-photon emission are briefly addressed.

1. Introduction

Sources of single photons are important building blocks for several quantum technologies. They are successfully used in quantum cryptography, computation, teleportation, and metrology. Many different systems have been studied for their use as sources of single-photon emission.[1] Solid-state single-photon emitters (SPEs) such as semiconductor quantum dots[2] or color centers in diamond[3] are of special interest since they can be monolithically integrated into photonic waveguides and cavities. Recently, bright and stable SPEs have been discovered in atomically thin transition metal dichalcogenides (TMDs),[4–8] other 2D van der Waals (vdW) materials,[9,10] and heterostructures[11] (Figure 1). The 2D nature of the host crystals offers a high mechanical flexibility and a localization of the SPE at or close to the surface. It enables new advantageous methods for the creation, localization, and control of SPEs, for example, via mechanical strain or their hybrid integration into photonic structures.

In this review, we summarize the state-of-the-art of single-photon emission from different types of emitters in layered vdW materials. After a brief introduction of basic aspects of single-photon emission and a short historical overview, we will summarize the basic properties of SPEs in different 2D vdW material systems. We will then address theoretical aspects associated with ab initio simulations of the defect centers and the role of the electron-phonon coupling for their spectral properties. After discussing the methods for the creation and localization of SPEs in 2D vdW materials, we will present our view on perspectives and possible applications.

1.1. Single-Photon Emission

An ideal SPE is characterized by the fact that at a given time only a single photon is emitted. Mathematically, this property is described by the second-order correlation function $g^{(2)}(\tau)$ of the photon field.[12] Considering for simplicity a single mode field with operators $a^{\dagger}(t)$ ($a(t)$) describing the creation (annihilation) of a photon at time $t$, this correlation function is given by[13]

$$g^{(2)}(\tau) = \frac{\langle a^{\dagger}(t)a^{\dagger}(t+\tau)a(t+\tau)a(t)\rangle}{\langle a^{\dagger}(t)a(t)\rangle\langle a^{\dagger}(t+\tau)a(t+\tau)\rangle}$$

which is independent of $t$ for stationary fields. In a coherent light field, the photons are uncorrelated giving rise to $g^{(2)}(0) = 1$ while thermal light exhibits photon bunching characterized by $g^{(2)}(0) = 2$. In fact, for any classical field $g^{(2)}(0) \geq 1$ is satisfied.[13] In contrast, an ideal SPE emits antibunched photons satisfying $g^{(2)}(0) = 0$, i.e., the probability of a simultaneous emission of two photons is zero. In a real experiment one always measures a finite, nonzero value. A measurement of $g^{(2)}(0)$ thus...
characterizes the purity of the single-photon field. Assuming a photon Fock state with \( n \) photons (\( n > 0 \)), one has\(^{[13]} \)

\[
g^{(2)}(0) = \frac{\langle a^\dagger a^\dagger a a \rangle}{\langle a^\dagger a \rangle^2} = \frac{n^2 - n}{n^2} = 1 - \frac{1}{n} \quad (2)
\]

Thus, \( g^{(2)}(0) = 0 \) for a one-photon Fock state while \( g^{(2)}(0) = \frac{1}{2} \) for a two-photon Fock state. Based on these values, single-photon emission is usually defined by \( g^{(2)}(0) < \frac{1}{2} \). Applications in the field of quantum technologies, however, often require much higher degrees of purity ranging from \( g^{(2)}(0) < 0.1 \) for quantum key distribution to \( g^{(2)}(0) < 0.001 \) for cluster-state quantum computing or all-optical quantum repeaters.\(^{[15]} \)

The measurement of \( g^{(2)}(\tau) \) is at the heart of the characterization of an SPE. Therefore, results for \( g^{(2)}(\tau) \) are provided in almost all experimental studies of SPEs. The standard measurement technique for this quantity is the Hanbury Brown and Twiss (HBT) setup, in which the optical signal is split by a beam splitter and sent to two detectors recording the coincidences as a function of the delay in the two pathways. In the case of continuous-wave excitation of the emitter, the HBT signal is characterized by a dip at \( \tau = 0 \) with a width determined by the lifetime of the emitter.\(^{[16]} \) In the case of a pulsed excitation, the HBT signal exhibits a series of peaks at multiples of the pulse repetition time with a reduced height of the peak at \( \tau = 0 \); this peak is completely absent for an ideal SPE.

While in semiconductor quantum dots, where single-photon emission has been studied for about two decades now,\(^{[16]} \) extremely high purities with \( g^{(2)}(0) \)-values as low as \( 7.5 \times 10^{-5} \) have been measured.\(^{[18]} \) Defects in layered vdW materials typically provide a large spreading and are still far from such values. Nevertheless, it has been shown that, e.g., by using post-processing treatments single-photon emission from defects in hexagonal boron nitride (hBN) can be purified and \( g^{(2)}(0) \leq 0.1 \) can be obtained.\(^{[19]} \) Using resonant excitation of WSe\(_2\) even a value below 0.002 has been achieved.\(^{[20]} \)

While for some applications, e.g., in quantum key distribution, an uncorrelated emission of pure single photons is sufficient, other applications such as linear-optical quantum computation also need the fact that subsequently emitted photons are identical in all measurable quantities. This property is reflected by the indistinguishability, which can be measured in a Hong–Ou–Mandel interferometer.\(^{[21]} \) Here, the emitted signal is split into two beams which are then recombined on a beam splitter. If two photons arriving from different sides on the beam splitter are completely indistinguishable they will always leave the beam splitter on the same side. Therefore, the coincidence count of the detectors at both outputs of the beam splitter vanishes in this case. If the photons are distinguishable in some quantity, they will not interfere and there will be coincidence counts. Highly indistinguishable photons have been demonstrated in the case of quantum dot SPEs.\(^{[22]} \) Many SPEs in vdW materials still suffer from phenomena like spectral jitter, which still limits the indistinguishability of photons created in this material class.

Finally, the brightness of an SPE is another important criterion for many applications. It is a measure of the efficiency of the creation and extraction of single photons, however, there is no unique definition of the brightness which often restricts the quantitative comparability of different results.\(^{[22,23]} \) A quantum light source with a high brightness is characterized by a high quantum efficiency, a sufficiently short lifetime of the emitter, and a high extraction efficiency of the emitted light. Particularly high quantum efficiencies of about 87% have been obtained from SPEs in hBN,\(^{[24]} \) which, together with the fact that in this material system single-photon emission is observed at room temperature, makes this class of emitters attractive for applications.

### 1.2. Discovery

Single-photon emission from localized emitters in 2D vdW materials has first been reported in the 2D semiconductor WSe\(_2\).\(^{[4–8]} \) The localized light emitters have been found to appear at edges (Figure 2a) of the atomically thin material\(^{[4,5,7]} \) or in folds.\(^{[6]} \) This finding suggested, that mechanical strain plays a major role in the creation or activation of the quantum light emitters, which makes them distinct from other solid-state SPEs and offers new possibilities for the deterministic creation and positioning as well as integration into nanophotonic structures. Shortly after, similar localized light emitters were discovered in other 2D semiconductors, such as MoS\(_2\),\(^{[25,26]} \) (although, no antibunching was demonstrated at that time), WS\(_2\),\(^{[27]} \) and in the gallium monochalcogenide GaSe\(^{[9]} \) (Figure 2b). In the TMD MoS\(_2\), localized emitters have been created by ion bombardment\(^{[28]} \) (Figure 2c) and most recently, SPEs emitting at telecommunications wavelengths have been created in MoTe\(_2\).\(^{[29]} \) The discovery of SPEs in the wide-bandgap vdW insulator hBN\(^{[10]} \) has also attracted considerable attention (Figure 2e). Recently, the family of quantum light emitters in 2D vdW materials was extended by excitons localized in Moiré superlattice potentials.\(^{[11]} \)

### 1.3. Basic Properties

#### 1.3.1. WSe\(_2\)

At cryogenic temperatures, the SPE energies lie between \( \approx 20 \) and \( 200 \) meV below the neutral free 2D exciton in...
The emission intensity of the 2D exciton is significantly reduced at the spatial position of the localized light emitter, which indicates that the 2D exciton is efficiently captured or funneled into the localized emitters. The photoluminescence (PL) spectrum of the emitters features a narrow line width (down to 100 μeV), especially if the monolayers are prepared free-standing (on holes) or on atomically flat hBN. Under resonant laser excitation, the fluorescence line width can be extremely narrow (<10 μeV). With increasing temperature, the emission line broadens due to the interaction with phonons (as discussed in Section 2.2) and the emitters typically disappear at a temperature above 35 K. Photon correlation measurements show a high single-photon purity with $g^{(2)} < 0.03$, which can be even further improved by resonant excitation down to $g^{(2)} < 0.002$.

A significant fine-structure splitting (FSS) of up to 0.8 meV was found, which indicates a confinement of excitons in an asymmetric potential. The two FSS split energy states are polarized perpendicular to each other. In addition, similar to self-assembled semiconductor quantum dots, the radiative cascade from the localized biexcitons has been observed in WSe$_2$ SPEs (see Figure 2d). Furthermore, magneto-optical measurements demonstrate a large Zeeman effect with g-factors between 9 and 12 and photoluminescence excitation (PLE) spectroscopy shows a large energy gap between the ground state emission energy and the first excited state.

**1.3.2. Other 2D Semiconductors: WS$_2$, MoSe$_2$, MoTe$_2$, MoS$_2$, and GaSe**

Similar SPEs have been found in other 2D semiconductors. In WS$_2$, they have been observed first in a light-emitting diode structure and they show similar strain activation as the SPEs in WSe$_2$. Furthermore, light emission from individual electrically excited atomic defects in WS$_2$ has been studied using scanning tunneling spectroscopy.

In MoSe$_2$ localized light emission with narrow emission lines has been observed, however, no antibunching was reported. The g-factor of these localized emitters was measured to be around 4, which is very close to the value of the g-factor of the 2D neutral exciton and significantly different from the observation in WSe$_2$. Only recently, single-photon emission has been confirmed by photon correlation measurements on site-controlled emitters.

SPEs in the near-infrared (NIR) spectral region have been created by strain engineering in the TMD MoTe$_2$. While in monolayers near-band-edge SPEs around 1.13 eV have been observed, the smaller band gap of multilayer MoTe$_2$ allows for the creation of SPEs emitting in the spectral range from 1200 to 1600 nm, covering the O–C telecommunication bands.

In the gallium monochalcogenide GaSe, single-photon emission has been related to strain induced by intrinsic selenium cluster intercalations. In this material system, localized
emission is observed even at room temperature, although antibunching has only been confirmed at cryogenic temperatures. Interestingly, antibunching is only detected for emitters which feature—besides the exciton—also emission from the biexciton (see Figure 2b).

While in other 2D semiconductors the appearance of localized photon emission has been found to be closely related to strain and to occur without the deliberate introduction of atomic defects, in MoS$_2$ photon emitters have been observed only after targeted creation by the formation of defects using a focused helium ion beam$^{[28,37,38]}$ (see Figure 2c). In contrast to the SPEs in the other TMDs, the emitters in MoS$_2$ exhibit rather long recombination times in the range of microseconds.

Until now, the origin of the single-photon emission in 2D semiconductors is under intense discussion. Some emitters are attributed to atomic defects$^{[28,39,40]}$ while in most cases a combination of a defect and a local strain distribution seems to be a crucial factor for the activation of SPEs.$^{[10]}$

### 1.3.3. hBN

In hBN, SPEs have been first reported in mono- and multilayer samples in the visible range around 2 eV (620 nm) using an optical excitation at 2.3 eV (532 nm).$^{[10]}$ The emission shows a narrow zero-phonon line (ZPL) for bulk and few-layer samples, while the emission in monolayer hBN is significantly broadened. Subsequently, quantum emission was reported in a larger spectral range in the visible (1.6–2.5 eV)$^{[41,42]}$ as well as in the deep UV (4.1 eV)$^{[44]}$ as well as in the deep UV (4.1 eV)$^{[44]}$. Furthermore, localized emission from color centers in the blue and UV has been reported.$^{[55,46]}$ Emitters are found in single crystals,$^{[10]}$ chemical vapor deposition (CVD) grown layers,$^{[47,48]}$ as well as nanopowder$^{[49,50]}$ samples of hBN. The SPEs in hBN are among the brightest SPEs in a solid-state crystal without an auxiliary photonic structure$^{[51]}$ and have high quantum efficiencies approaching 87%.$^{[52]}$ The emission is stable from cryogenic temperature up to room temperature and even high-temperature single-photon emission up to 800 K was demonstrated.$^{[52]}$

Besides the sharp ZPL, the emission spectrum of the emitters exhibits two prominent sidebands 150 to 200 meV below the ZPL$^{[41,51,53–55]}$, which originate from optical phonon-assisted emission.$^{[56]}$ The line width of the ZPL increases exponentially with temperature due to the coupling with acoustic phonons$^{[56]}$ (see also Section 2.2). The emission is linearly polarized, suggesting an in-plane dipole. However, the orientation of the emission and absorption dipole are not always identical,$^{[53,57]}$ and no clear correlation between the emission polarization orientation and a crystallographic axis was found.$^{[53]}$ Interestingly, the energy of the ZPL shows no shift with the magnetic field,$^{[49,58,59]}$ but the PL intensity can vary with the magnetic field.$^{[58]}$

Near-resonant PLE scans of individual SPEs demonstrate Fourier-transform limited absorption line widths below 100 MHz for some emitters.$^{[60,61]}$ For the emitted photons, first-order coherence measurements on the ZPL at 5 K revealed coherence times in the order of 50 to 100 ps,$^{[62,63]}$ corresponding to a spectral width in the GHz range. The coherence time and the corresponding spectral width are limited by spectral diffusion on the micro- to millisecond time scale.$^{[62–65]}$ On a short timescale for correlation times below 1μs (i.e., only correlating photons which are emitted within a microsecond) a photon coherence time of 434 ps was reported.$^{[63]}$ Rabi oscillations have been observed in the second-order correlation function for resonant excitation, demonstrating the potential for optical coherent control of hBN SPEs.$^{[65]}$ An important challenge for future applications is the reduction of the spectral jitter. Special excitation schemes, such as anti-Stokes excitation,$^{[66]}$ are a possible way to decrease the spectral diffusion.

Despite the numerous studies of SPEs in hBN, the atomic structure and therefore the energy-level structures of the quantum emitters are still unclear. The observation of bunching in the second-order correlation function of the emitted photons suggests the existence of intermediate (metastable/dark) states between the excited state and the ground state.$^{[67,68]}$ Multicolor excitation with a green and a blue laser further indicates photoinduced switching between a bright and a metastable dark state.$^{[68]}$ Recent reports suggest carbon as a key component of the quantum emitters.$^{[69,70]}$ However, it is not clear, whether a single crystallographic defect center can explain all experimental findings or if different types of defects cause the large spectral range of transition energies.

### 2. Theoretical Aspects

The study of SPEs in layered vdW materials involves various theoretical aspects, which combine different fields of condensed matter physics and optics. In the most simple case, an SPE is described by a two-level system characterized by the transition energy and the dipole matrix element, which are typically adjusted to the values obtained from the experiment. This is by definition an ideal SPE since at a given time only one photon can be emitted and the spectrum is given by a single, homogeneously broadened spectral line. Real SPEs, which are in the focus of this review, are realized by defect structures (strain or point defects both perturbing the periodic potential of the lattice) in a solid-state matrix and therefore deviate from the ideal case both in the spectral and the temporal domain. To prove the physical nature of a defect, ab initio calculations are required which provide the level structure but also properties like the degree and orientation of the polarization of the emitted light. Defects in a solid-state matrix are not isolated from the crystalline environment but necessarily couple to their dynamical degrees of freedom, notably the phonons. This coupling can give rise to pure dephasing and characteristic sidebands in the optical spectra. For this reason, a detailed understanding of the spectral properties requires a model including the electron–phonon interaction. In the following, we will review recent work addressing these aspects for SPEs in layered materials.

#### 2.1. Ab Initio Simulations for the Local Structure of SPEs

The transition energies of the SPEs in TMDs appear energetically only slightly below the bright optical emission of the monolayer excitons in unperturbed samples. As explained in Section 3.1, SPEs are likely found in locally strained regions of the crystal and systematic strain studies of monolayer excitons suggest that the SPE energies might correspond to a strain shift of a few
percent. First theoretical investigations have considered local potential wells induced by strain.[71] However, quantization energies in such potential wells of approximately 100 nm diameter do not support the single-photon emission nature because higher excited states would be too close in energy. Especially the fact that quantum emission is found for further increasing temperatures[30] contradicts this hypothesis. To solve this issue, more recent studies suggest a combination of local strain distribution and a local atomic defect.[72] As depicted in Figure 3a in such a configuration, the potential well could work in a twofold way. On the one hand, it funnels the excitons toward the defect making an occupation more likely. On the other hand, the strain provides a coupling between the monolayer exciton states and the localized states of the defect.

Independent theoretical studies suggest that nanobubbles in TMD monolayers could support localized excitonic emitters.[73] The bubble geometry introduces localized strain but also an inhomogeneous dielectric environment that supports the potential formation of SPEs. First experimental studies have recently confirmed microscopic strain distributions and exciton localization in such structures[74] but confirmation of photon antibunching is currently still pending.

Some other ab initio studies also suggest dislocations as SPE sources.[75] It was shown that reasonable 5–7 and 4–6 dislocations in WSe2 should support linearly polarized SPEs. However, such dislocations are likely to appear in grain boundaries[76] but SPEs have not yet been reported to appear predominantly at these distinct positions.

The majority of theoretical studies on SPEs in layered materials focus on the investigation of possible energies for the confined quantum states. In hBN, the optical transition energies appear at much lower energies than the intrinsic bandgap of 6–7 eV[10,77] It is, therefore, very likely that the SPE is an atomistic defect structure similar to those known from other insulators like nitrogen-vacancy (NV) centers in diamond.[78] So far the real atomic structure (structures) of hBN SPEs is (are) not finally identified. To solve this issue, the first ab initio studies considered various atomic defect structures and calculated their optical transition energies.[78–83] One such example is shown in Figure 3b for the V

From Ref.[84], where the defect’s response on external strain is studied (see Section 4.2 for details). The picture shows the atomic defect structure with its local phonon mode in the top and excited state wave functions with C2v (left) and C3 (right) symmetry in the bottom. The possible transition energies constitute the first and most obvious criterion for the identification of the defect (defects) present in the physical samples. A second criterion is the linear polarization in absorption and emission of the bright ZPL. In this context, group-theoretical aspects are often used that rely on the symmetry of the considered defect structure.[85] Experiments have also shown that the level structure likely consists of at least one optically active excited state and one additional dark excited state energetically below the bright one, which is a possible third criterion of the emitter structure. Almost any considered defect structure should possess several dark states and therefore support this requirement. A fourth criterion is the Stokes shift, i.e., the energy difference between the same spectral feature in absorption and emission. Experiments show that the Stokes shift of hBN emitters is in the range of a few meV, if even present at all. Recent ab initio studies report a Stokes shift of several hundred meV for the V

2.2. Electron-Phonon Coupling and Spectral Shape

PL spectra of SPEs in layered materials exhibit characteristic asymmetric ZPLs.[28,77] These features typically stem from the coupling to acoustic phonons, as it is well known from semiconductor quantum dots.[86] An established theoretical approach to simulate these spectral features is the independent boson model where the absorption spectrum is given by the Fourier transform of the time-dependent linear susceptibility[87]

\[
\chi(t) = \exp\left\{ \sum_j \sum_k |\gamma_{jk}|^2 \left[ e^{-i\omega t} - n_j(k) e^{-i\omega t} - 1 \right] \right\}
\]

(3)
It describes the optical spectrum of an SPE by taking the phonon dispersion $\omega_{j,k}$, the phonon occupation $n_j(k)$ determined by the Bose–Einstein distribution, and the phonon coupling strength $\gamma_{j,k}$ for a given mode $j$ into account. Originally developed for impurities the model is routinely applied to calculate optical spectra and dynamics of semiconductor quantum dots. The spectrum can be expressed in terms of the sometimes more instructive – phonon spectral density $J_j(\omega) = \sum_k |\gamma_{j,k}|^2 \delta(\omega - \omega_{j,k})$. In principle, the phonon spectral density is determined by the involved wave functions of the transition, the specific coupling mechanism, and the phonon dispersion. The model was used to calculate the PL spectra of SPEs, particularly in MoS$_2$ as shown in Figure 4a for different temperatures, where the deformation potential coupling and s-like orbitals were assumed. However, in many examples, it is sufficient to consider a heuristic phonon spectral density $J_j(\omega) \approx \omega^2 e^{-\omega/\omega_0}$ to retrieve a good agreement with measured PL spectra. In this approach, $\omega_0$ is a characteristic cut-off frequency that mainly reflects the emitter size and $n_j$ is determined by the dimensionality of the system. This simplified method was successfully used to model the PL spectra of ultraviolet hBN emitters (Figure 4b).

Especially the spectra of hBN color centers possess much richer phonon sideband (PSB) structures. It is known from other color centers like NV centers in diamond that PSBs can have a strong impact on the PL spectrum due to an efficient contribution of local mode oscillations. For hBN emitters, such confined phonon modes are expected to contribute to the optical spectra, too. Also in this context, ab initio studies have been used to determine the characteristic vibronic spectrum of different emitter structures. The predicted energies should line up with specific sidebands in the PL spectrum. This renders another criterion for the identification of the defect structure, because every atomic configuration has its unique local mode spectrum making it a fingerprint, like the excited state level-structure.

The most pronounced PSBs in the hBN spectra are likely not related to local modes. For most samples, two strong peaks appear between 165 and 200 meV below the ZPL as shown in Figure 4c, which lines up perfectly with the LO phonon energies of the hBN bulk crystal. Thereby, these PSB energies should not be unique for a specific atomic defect structure but rather more or less the same independent of the exact emitter structure. Nevertheless, the actual shape of the PSBs given by broadenings and relative peak heights can be used to gain further insight into the defect characteristics. To clearly identify these two maxima as PSBs belonging to the same emitter one can have a closer look at the energy range between 300 and 450 meV below the ZPL as highlighted by the inset in Figure 4c. One finds a triple peak structure that perfectly lines up with the three possible two-phonon processes of the two LO modes LO$_1$ and LO$_2$ as labeled in the plot. All spectral features agree almost perfectly with the simulations in the independent boson model. This finding is in contrast to the suggestion that the PSB marked as LO$_2$ stems from the same LO mode but belongs to another ZPL. In this scenario the second LO PSB would only exhibit two peaks. However, the triple peak structure is regularly found in various emitters proving the coupling of two different LO phonon modes.

3. Creation and Localization of SPEs

3.1. Local Strain Distribution

While the first reports on SPEs in TMDs mentioned an apparently random positioning, preferably at the edges of monolayers, the following research focused on their systematic positioning. It rapidly turned out that the generation of localized strain distributions is a suitable tool to localize SPEs. To this end, pre-patterned substrates are used to introduce bending in the monolayer. The approaches reach from gapped substrates via pillar arrays to gapped bar structures. This method already allowed to create regular patterns of emitters and was later also adapted to hBN.
crystals. Likewise, SPEs in GaSe were found where the layers form bulges due to deformations of the substrate (Figure 5c).

To estimate the strain introduced by the bending, a common approach is to apply a classical continuum model describing a thin plate. After determining the morphology of the structure, the strain can directly be calculated from the local bending. Typical dimensions of the strained area are in the range of several tens to hundred nanometers, which allows to reach maximum strain values of a few percent. Details on the impact of the local strain distribution for the creation or localization of SPEs have been discussed in Section 2.

3.2. Defect Creation by Irradiation

Ion beam implantation techniques are widely used to create optically active quantum emitters, commonly referred to as color centers, with high spatial resolution in materials including diamond[100–103] and sodium chloride.[104] 2D vdW materials, such as MoS2, can help to confine the stochastic interaction between the ion beam and the host lattice, providing an intrinsic sub-nanometer positioning of the generated defects in the vertical direction and a lateral broadening of only a few nanometers.[28,105–109] Focused ion beams of gold,[110] xenon,[111] argon,[112] and helium[106,107] were shown to provide a lateral precision even below 10 nm for patterning single-layer MoS2 (see Figure 2c). Importantly, helium ion beam exposure was shown to generate SPEs in single-layer MoS2.[28,37,113] The quantum emitters exhibit microsecond lifetimes at low temperatures, with a high generation yield of 18% of single SPEs at specific atomistic sites and close to 100% within areas of >0.1 μm2.[113] and an improved spectral homogeneity when the MoS2 layer is encapsulated in inert hBN crystals.[113] (Figure 5d). Recent annealing experiments combined with scanning tunneling microscopy studies demonstrated that the quantum emitters are most likely pristine sulfur vacancies without being passivated by oxygen.[28,106,115] The helium ion beam allows generating quantum emitters in already assembled heterostacks with the mentioned high spatial resolution, as demonstrated by gate-tunable quantum emitters in MoS2-hBN stacks with graphene gates.[108]

3.3. Defect Formation by Annealing

Thermal annealing is known to activate SPEs in hBN[10,116] (Figure 5e). Typically, annealing at a temperature of 850 °C or higher[117] in vacuum, in an inert gas (e.g., Ar) or in an oxygen atmosphere is utilized. Either as-synthesized hBN[10] is annealed to activate intrinsic defects or annealing is performed after deliberate creation of defects by electron-beam irradiation,[118,119] neutron irradiation,[120] bombardment with ions,[121,122] or chemical etching.[123] Creation of edges by a focused ion beam,[124] intense laser beam irradiation[125] or mechanical deforming and damaging[126] and a subsequent annealing leads also to the formation of SPEs in hBN, allowing for a deterministic positioning. For pristine hBN nanopowder, the number of optically active SPEs was found to increase by 50%[106] after annealing. Furthermore, the thermal treatment increases the spectral stability of the SPEs.[123]

The mechanism behind the activation of SPEs by thermal annealing is still unknown. Theoretical calculations predict that at a temperature of 850 °C, the boron vacancy in hBN is mobile,
while the nitrogen vacancy and other defect atoms are less likely to migrate in the crystal lattice. Interlayer interstitials are also assumed to be mobile due to the low interlayer bond energies of the layered material. However, changes in the electron paramagnetic resonance (EPR) spectrum of heavily neutron-irradiated hBN samples at annealing temperatures above 550 °C indicate that structural changes or migration of defects or vacancies already starts in the temperature range between 600 and 800 °C. Furthermore, the large surface-to-volume ratio of the 2D vdW material enables also the direct incorporation of atoms from the gas phase, e.g., annealing in a carbon-rich atmosphere leads to the formation of carbon-related defect centers in the hBN crystal.

4. Perspectives and Applications

4.1. Quantum Optics

To further advance quantum technologies—and especially quantum communications—fully integrated quantum optical circuits including high-quality single-photon sources and single-photon detectors are required. One of the biggest promises of SPEs in 2D vdW materials is the ease of hybrid integration, i.e., combining the 2D vdW materials and the SPEs therein with plasmonic metal nanostructures or dielectric integrated nanophotonic structures. The 2D vdW material hosting the SPE is typically transferred via stamping techniques onto the prefabricated nanostructures. Several works exploit strain for the activation of SPEs, which enables the deterministic creation of SPEs directly at the desired position on the prefabricated plasmonic or photonic structure. In many structures, nanoscale control over the distance between the plasmonic or photonic structure and the SPE is required to achieve a high coupling efficiency. Due to the atomically thin nature of the host material, SPEs in 2D vdW materials can be placed within atomic distance of the coupled photonic structure.

4.1.1. Coupling to Resonant Cavities

A key strategy to improve the quality of the single-photon emission is the coupling of the emitters to resonant cavity structures. The Purcell effect leads to an enhanced spontaneous emission rate and funneling of the emission into the cavity mode. Thereby the collection efficiency and brightness of the single-photon source is improved, the susceptibility of the SPE to spectral jitter is reduced and the operating temperature can be increased. Different types of nanophotonic structures—from dielectric microcavities via nanoantennas to plasmonic resonators—have been employed to modify the emission properties of SPEs in WSe2 and hBN.

Quantum emitters in 2D vdW materials are well suited to be integrated into tunable open microcavities consisting of a hemispherical and a flat dielectric Bragg mirror (DBR), of which the distance can be precisely controlled by a piezoelectric actuator (Figure 6a). The placement of the 2D vdW material at the surface of the flat DBR with a low refractive index termination ensures longitudinal alignment to an antinode of the mode. Depending on the radius of the hemispherical mirror in the range of a few micrometer, small mode volumes down to 1.76 λ3 have been achieved. In combination with quality factors in the order of Q ≈ 104, enhancements of the spontaneous emission rate with Purcell factors of Fp ≈ 4 for an hBN SPE and Fp ≈ 16 for an WSe2 emitter were demonstrated.

![Figure 6](image-url)
A hybrid approach to couple an SPE to a resonant cavity is to put the 2D vdW material directly onto photonic structures such as a Si$_3$N$_4$ microdisk optical resonator$^{[130]}$ (Figure 6b) or a Si$_3$N$_4$ 1D photonic crystal.$^{[118]}$ This can be done after fabrication of the photonic structures as in the case of the microdisk resonator, where a 20 nm-thick hBN flake was placed on the resonator and local strain at the edge activates the emitters, or by integration of an hBN flake on a Si$_3$N$_4$ substrate prior to the fabrication process.$^{[138]}$ Here, the creation of edges in the hBN during the etching of the structures leads to the formation of SPEs. In both cases, clear signatures of the coupling between the cavity mode and the SPE have been observed.$^{[130,138]}$ Similarly, an Al$_{0.31}$Ga$_{0.69}$As circular Bragg grating bullseye cavity covered by a WSe$_2$ monolayer can significantly enhance the PL from a strain-defined SPE in the center of the structure (Figure 6c) with a Purcell factor of $F_P \approx 5.$$^{[139]}$

Dielectric nanoantennas made from high-refractive-index materials can confine broadband optical modes with very small mode volumes with the advantage of low nonradiative losses$^{[132]}$ (Figure 6d). Covering the nanoantennas with WSe$_2$ leads to the activation of SPEs coupled to the optical mode, which is found to enhance the PL by a factor of $10^2$ to $10^4$ compared to strain activated SPEs by a low-refractive-index SiO$_2$ nanopillar.$^{[140]}$

Plasmonic nanostructures concentrate light to subwavelength dimensions and are therefore well suited to efficiently couple SPEs to propagating light fields. Already a rough metallic surface coated with a thin 3 nm dielectric Al$_2$O$_3$ layer can serve as a platform to activate SPEs in WSe$_2$ due to strain and significantly reduce their PL decay times due to the presence of the plasmonic structure.$^{[97]}$

Propagating surface plasmon polaritons (SPP) in plasmonic nanostructures such as a silver nanowire on a glass substrate,$^{[141]}$ in porous metallic networks,$^{[142]}$ or plasmonic slot waveguides$^{[133,134]}$ coupled to an SPE in WSe$_2$ enabling remote SPP-mediated excitation or routing of single plasmons generated by the SPE over a distance of several micrometers (Figure 6f). In all these experiments, the positioning of the emitter by inherent strain activation by the plasmonic structure is crucial for the efficient coupling.

Plasmonic nanostructures, e.g., gold nanorods$^{[143]}$ or a thin gold layer on silicon nanopillars$^{[144]}$ covered with a WSe$_2$ monolayer yield also the formation of SPEs by strain coupled to enhanced light fields. Similarly, the SPE activation in hBN can be enhanced by transferring hBN on silver or gold nanopillars.$^{[131,135]}$ By combining a metallic nanostructure with a planar metal mirror, plasmonic nanocavities can be formed in which the atomically thin monolayer is sandwiched, allowing for an excellent optical coupling.$^{[145]}$ The strong reduction of the PL decay time leads to an increase of the working temperature up to 160 K$^{[146]}$ (Figure 6e). Finally, metallo-dielectric structures coupled with hBN emitters yielded near-unity collection efficiency of the photons.$^{[147]}$

4.1.2. Coupling to Waveguides

One crucial idea of hybrid on-chip integration is to use the mature integrated optics technology to fabricate wave guiding structures and couple them with highly efficient SPEs. However, efficient coupling between an SPE and the guided mode of a waveguide is still challenging, since efficient coupling requires a deterministic positioning of the SPE to achieve an overlap of the guided mode with the wavefunction/dipole of the SPE. Three different approaches have been implemented: 1) evanescent coupling of the SPE to the waveguide mode by placing the emitter on top of the waveguide, 2) a hybrid approach, where the host material of the SPE reshapes the optical mode to increase the coupling efficiency, and 3) a monolithic approach, where the optical mode is guided in the host material of the SPE.

The SPEs are WSe$_2$ are activated by strain, which can be induced by placing a monolayer of WSe$_2$ onto a steep edge of a pre-patterned substrate. By stamping a monolayer onto a Si$_3$N$_4$ waveguide,$^{[148,149]}$ SPEs appear at the edge of the waveguide and couple to the waveguide (Figure 7a). However, the optical waveguide mode has only a weak overlap with the dipole at the edge of the photonic structure, therefore the coupling efficiency is still small.$^{[148,149]}$ In the future, optimized waveguide geometries or the introduction of cavities might allow to overcome this issue and enhance the coupling.

SPEs in hBN are especially interesting for integrated quantum optics because of their wide range of operation wavelengths and the quantum emission at room temperature.$^{[10,42]}$ A straightforward approach to couple the emitted photons into an optical fiber is attaching an hBN flake directly onto the end facet of a multimode fiber.$^{[150]}$ Similar coupling efficiency of around 10% was achieved, when coupling single photons from hBN into a tapered fiber$^{[151]}$ (Figure 7c). For on-chip coupling into integrated waveguides on AlN or Si photonics, the hBN emitter can be positioned on the prefabricated waveguide$^{[129]}$ (Figure 7d) or—vice versa—the waveguide is deterministically fabricated on top of an hBN flake.$^{[152]}$ However, the coupling efficiency is still far from unity and more advanced structures, such as suitable cavities are highly desired to reach near-unity coupling efficiencies.

For GaSe SPEs, efficient coupling was achieved by exploiting the optical properties of the 2D vdW material (hybrid approach)$^{[153]}$ By placing this high-refractive-index material on top of a Si$_3$N$_4$ waveguide, the guided mode is pulled out of the waveguide into the GaSe (Figure 7b). Only light from SPEs with significant spatial overlap between the guided mode and the dipole of the emitter coupled into the waveguide with an efficiency up to 21%.$^{[153]}$

Another approach of coupling of an SPE to an on-chip waveguide is achieved by monolithic integration of the SPE into a waveguide, i.e., fabricating a waveguide entirely from the host material of the SPE. Since hBN is a wide bandgap material with a high refractive index, the material is well suited for fabricating nanophotonic structures.$^{[154]}$ Recently, the monolithic integration of an hBN SPE in an hBN waveguide was demonstrated and a maximum coupling efficiency for this structure of the SPE emission into the waveguide was calculated to be 37%.$^{[155]}$ (Figure 7e).

4.2. Remote Control

External control of the properties of SPE is important for the implementation of quantum optoelectronic devices. Electrical contacting can be used to excite and tune the optical response of the SPEs in WSe$_2$. By embedding WSe$_2$ between two graphite...
electrodes insulated by thin hBN layers, electric-field-tunable devices have been built. The localized emitters in WSe$_2$ show a pronounced Stark effect, which can be used to tune the exciton transition energy.[156] Furthermore, also the FSS[157] is susceptible to the electric field. By additionally contacting the monolayer, a charge-tunable device has been created in which localized emitters can be tuned from an exciton to a trion state.[158] By injecting current into the WSe$_2$ layer, electrically pumped SPEs have been demonstrated.[27,159]

Already the hBN crystal has a strong polarity, which is also found in the properties of the embedded SPEs. By applying a constant electric field the energy of the optical transition of the emitter is shifted. This Stark effect was on the one hand reported for a geometry sensitive to the dipole orientation out of the hBN layers’ plane,[160] obtaining a shift of 15 meV (V/nm)$^{-1}$. In contrast, in Ref. [161] an in-plane geometry was used that resulted in a significantly larger energy shift of 43 meV (V/nm)$^{-1}$.

These findings together suggest that the emitter’s dipole is oriented predominantly in the plane of the hBN crystal but has a non-vanishing out-of-plane component.

While local strain can be crucial for the activation of SPEs in 2D vdW materials,[72] externally applied strain is also a viable tuning method for WSe$_2$ SPEs[162,163] as well as hBN emitters.[164,165] Compression or expansion of the host crystal lattice causes a change due to the deformation potential coupling, which describes how electronic states are shifted under influence of a constant strain. One example of a controlled strain application is schematically depicted in Figure 8a, where a bendable substrate is used to stretch the upper surface. On this surface, SPEs in WSe$_2$ are created by a locally patterned surface (see Section 3.1 for details). The applied strain leads to a shift of the transition energy of the SPEs of 50[162] and 120 meV%[163] for WSe$_2$ emitters. For hBN emitters, a much smaller transition energy shift of roughly 1–13 meV % was reported.[164,165] The strain field of surface acoustic waves (SAWs) allows for a dynamic modulation of the emission lines resulting in intensity variations and oscillations of the emission energy with an amplitude up to 2.5 meV.[166,167]

4.3. Optomechanics

Shortly after the discovery of graphene in 2004, layered materials started gaining attention as mechanical resonator systems. Suspended graphene sheets have been realized in their monolayer[168] and multilayer form[169] and charge currents were used to drive and probe the resonators’ mechanical modes. Such drum structures have also been realized for TMD monolayers.[170–172] The strong optical absorption in these materials allows to interact optically with the mechanical excitation of the system. While typical membrane geometries are round with characteristic Bessel-shaped mode profiles, also other geometries are possible, like rectangles.[173] Layered materials provide a large flexibility to tailor the mechanical properties by designing the membrane’s shape, size, and the number of used layers.[170]

As it has been demonstrated that SPEs in layered materials respond to mechanical strain,[163] some works have proposed to incorporate single emitters into vdW drum structures to generate quantum optomechanical systems. In Ref. [174], an hBN resonator coupling to an SPE in the membrane is suggested enabling an optical excitation scheme to create a
multicomponent Schrödinger cat state in the mechanical mode. In a similar approach, the system depicted in Figure 8b is considered and a quantum transducer that transfers single microwave photons to visible photons is simulated. The easy processability of the layered materials further allows to combine the layered materials with traditional resonator structures, e.g., in the form of a microdisk. Inspired by the rich work on the optomechanics of other quantum emitters like quantum dots or diamond color centers also vdW-based platforms are promising candidates for the interplay between the mechanical system and the optical or spin excitations of SPEs.

4.4. Defect Functionality in 2D Semiconductors Beyond Single-Photon Emission

Beyond their functionality as SPEs, nanostructured and defect engineered 2D TMDs play an important role in nanoelectronics, thermoelectrics as well as catalysis. Chalcogen vacancies for instance significantly reduce the Schottky barrier height in TMD/metal junctions important for realistic two- and three-terminal structures, such as field-effect transistors and are responsible for hopping transport in the low-doped regime. It has been demonstrated that MoS2 memtransistors can be fabricated by localized defect creation. Layered vdW materials are promising materials for thermoelectric applications particularly due to their anisotropic nature for charge and heat transport. The thermal conductivity can, for instance, be effectively tuned by strain and defect engineering. TMDs are also suitable for heterogeneous catalysis. For instance, monolayers of MoS2 hold enhanced catalytic activity while being highly stable immersed in aqueous electrolytes under intense light illumination. The edges of pristine MoS2 are the catalytically dominating sites, whereas the pristine basal planes are typically inactive (Figure 8c). Moreover, defect-engineered TMDs might become an interesting building block for the realization of 2D electrical, optical, or electrochemical systems for neuromorphic computing.

5. Conclusions

We have reviewed physical properties, theoretical concepts, and fabrication techniques of SPEs in layered van der Waals materials and discussed perspectives for their application in various fields of physics and technology. To summarize, in Table 1, we have collected typical values of some key properties of these SPEs in different 2D vdW material systems and heterostructures.

As has been seen in the different sections of this review, there are still many open questions and plenty of opportunities for improvements of functionalities and for further applications. Nevertheless, it can be clearly said that since their discovery in 2015, SPEs in 2D vdW materials have already come a long way in this short amount of time.

Table 1. Typical values of some key properties of SPEs in different 2D vdW material systems and heterostructures.

| System | Property — | Energy [eV] | PL lifetime [ns] | Operational temperature | Lateral positioning precision [nm] | Refs. |
|--------|------------|-------------|-----------------|------------------------|-----------------------------------|-------|
| WSe2   | (local strain) | 1.5—I.6    | ≈ 5 [from g2(r)] | cryog.                  | ≈ 100 (pillar diam.)             | [30]  |
| MoSe2  | (local strain) | 1.6         | 0.2             | cryog.                  | ≈ 50 (indent. diam.)             |       |
| MoS2   | (He ion microscopy) | 1.7—I.8    | 2000            | cryog.                  | ≈ 10 (He beam)                   | [113] |
| WS2    | (local strain) | 2.0         | ≈ 1.4 [from g2(r)] | cryog.                  | ≈ 100 (pillar diam.)             | [27,34] |
| MoTe2  | (local strain) | 0.8—1.1    | 22              | cryog.                  | ≈ 150 (pillar diam.)             | [29]  |
| GaSe   | (local strain) | 1.9         | 7               | cryog.                  | ≈ 20 (Se cluster)               | [9]   |
| Moire (MoSe2/WSe2) | 1.4         | 12           | cryog.           | ≈10—100 (Moire unit cell)   | [11]  |
| hBN (nanocryst., flakes) | 1.2—4.1    | ≈ 2          | room            | ≈ 150 (crystal size)         | [41,43,44] |
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Conflict of Interest

The authors declare no conflict of interest.

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defect states, hexagonal boron nitride, single-photon emitters, transition metal dichalcogenides, van der Waals materials

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