

Excitonic emission in van-der-Waals nanotubes of transition metal dichalcogenides

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ABSTRACT: Nanotubes (NTs) of transition metal dichalcogenides (TMDs), such as MoS₂ and WS₂, were first synthesized more than a quarter of a century ago; nevertheless, many of their properties have so far remained basically unknown. This review presents the state of the art in the knowledge of the optical properties of TMD NTs. We first evaluate general properties of multilayered TMD crystals, and analyze available data on electronic band structure and optical properties of related NTs. Then, the technology for the formation and the structural characteristics of TMD NTs are represented, focusing on the structures synthesized by chemical transport reaction. The core of this work is the presentation of the ability of TMD NTs to emit bright photoluminescence (PL), which has been discovered recently. By means of micro-PL spectroscopy of individual tubes we show that excitonic transitions relevant to both direct and indirect band gaps contribute to the emission spectra of the NTs despite the presence of dozens of monolayers in their walls. We highlight the performance of the tubes as efficient optical resonators, whose confined optical modes strongly affect the emission bands. Finally, a brief conclusion is presented, along with an outlook of the future studies of this novel member of the family of radiative NTs, which have unique potential for different nanophotonics applications.

1. Introduction

Allotropes of a 2D material, which are either a flat monoatomic layer or such a layer folded into a nanotube (NT), can possess essentially different optical properties. A well-known example of that are graphene and carbon NTs, representing various allotropes of carbon.^[1] One could expect similar behavior for inorganic NTs made from transition metal dichalcogenides (TMDs), such as MoS₂ and WS₂, in which the monolayers are held together by weak van der Waals (vdW) bonds.^[2-7] Interestingly, the carbon NTs were discovered as a new physical object in 1991.^[8] The TMD NTs synthesized from the vapor phase were reported around the same time, in 1992.^[2] However, their fates turned out to be completely different. After the initial elucidation of general physical properties of both, the interest to the carbon NTs was first stimulated by the discovery of luminescence from an individual tube,^[9] and warmed up further by the generation of quantum light.^[10] Naturally, that paves a road to their promising applications in nanophotonics and quantum technology.^[11]

As for the synthesized TMD micro- and nanotubes (for short, we use further the notation “NT” for both when sizes are not important), they were proposed for different applications in mechanics,^[12] in optoelectronics as detectors,^[13] in electronics as transistors,^[14] and also in tribology.^[15] Similar to other inorganic NTs, they can be used in nanofluidics for non-destructive interaction with a living cell.^[16] However, their application in nanophotonics as light emitters was never discussed because of the lack of data on their luminescent properties. It was not clear until recently whether they can emit light at all, not to mention what kind of radiation they exhibit – intense direct band gap exciton emission, as in a single TMD monolayer,^[17] or weak emission of a momentum-forbidden indirect exciton as in a bulk TMD crystal.^[18] It looks amazing in relation with nanostructures made of the TMD 2D materials, which became so popular after the observation of the indirect to direct band gap crossover in the monolayer limit yet in 2010.^[19]

For other vdW tubular structures, the situation was not so striking. For instance, the emission was observed from HfS₂ NTs,^[4] boron nitride NTs,^[20] and also from nanoscrolls fabricated by rolling up the MoS₂ monolayers.^[21] On the contrary, the studies of chemically synthesized MoS₂ and WS₂ NTs were focused on such characteristics of tubes ensembles as absorption^[22] and optical limiting, i.e. nonlinear saturation of light transmittance at high incident intensities.^[23] Theoretically, it was predicted that TMD NTs, independently on folding, should be semiconducting with a band gap smaller than in a bulk crystal.^[24,25] Also, it was noticed that multiwalled NTs must inherit the optical properties of the bulk crystal, i.e. exhibit the weak emission typical of momentum-forbidden indirect band gap transitions. This prediction is in line with the common opinion on the low radiative ability of the TMD layered crystals, supported by

experimental data.^[18] Contrary to these anticipations, bright excitonic emission from individual NTs has been recently discovered at the Ioffe Institute.^[26,27]

Here, we review data available regarding the technology and the structural properties, as well as the optical properties of TMD NTs. The layout of this paper is as follows. In section 2, basic optical properties of layered vdW TMD crystals and nanostructures are described. We believe that this collection of data on thin multilayer structures can be useful for understanding the optical properties of the related multiwalled tubes. In section 3, we consider the electronic band structure and the previously known optical properties of TMD NTs and of related curved nanostructures. Section 4 presents the formation technology and the structural characteristics of TMD NTs, focusing on those that are synthesized by chemical transport reaction (CTR). We describe some of the experimental details of our micro-spectroscopy studies of individual NTs in section 5. The lately discovered radiative properties of the single NTs are reviewed in section 6, where we present micro-photoluminescence (mPL) data obtained with spatial and temporal resolutions. They indicate that the emission spectra of NTs contain, as a rule, two bands related to the recombination of both direct and indirect band gap excitons. We highlight that the direct exciton emission is bright enough despite the large thickness of the walls of the tubes containing several dozens of monolayers. In section 7, we demonstrate that the vdW tubes can act as optical resonators and that the emission of both the bands can be selectively enhanced by coupling to the confined optical modes. The Conclusions and outlook of the NTs studies are presented afterwards.

2. Multilayer MoS₂ and WS₂ crystals and nanostructures

The studies of TMD layered crystals and nanostructures have a long, more than a half of century, history. Systemized earlier results can be found in the review of Wilson & Yoffe.^[28] The TMD family comprises about 40 compounds of MX₂ type, where M is a transition metal and X represents a chalcogen. The slabs of three atomic layers X-M-X, with internal covalent bonds, are linked together by weak vdW forces. The TMDs crystallize into different polytypes, determined by the slab stacking and the coordination symmetry of the metal atoms. The hexagonal 2H polytype contains two slabs with the second one rotated with respect to the first by $\pi/3$ around the axis perpendicular to the stacking. In the 2Hb case, the layers in the unit cell are displaced so that the M atoms of one layer are directly above the X atoms of the other layer. The repeating cell of the 3R polytype composes the three slabs mutually translated in plane with a shift. In both, 2H and 3R, metal atoms are surrounded by chalcogens forming a deformed trigonal prism coordination. The 1T polytype composes of one slab only but with octahedrally coordinated metal atoms. The detailed description of the polytypes can be found in several

reviews.^[28,29] In this work, we focus on two layered semiconductors – MoS₂ and WS₂. Their natural crystals have 2H preferable stacking, while the crystals grown by transport reaction can have the 3R stacking as dominant.^[28] Most of the published data on optical properties concern MoS₂, probably because the lowest dark exciton states in WS₂ complicate data analysis.^[30] Besides, MoS₂ has a particular significance for the modern 2D physics following the experimental observation of the direct band gap in its monolayers.^[19]

Theoretically, the electronic band structure of bulk MoS₂ was analyzed using first-principles calculations. It was predicted that the band gap is indirect with a value of ~1 eV^[31] in reasonable agreement with experimental data. The modification of the band structure from the bulk to the monolayer results from the strong quantum confinement in 2D materials.^[32] The modern view on the band structures of MoS₂ mono- and multilayers with 2H stacking can be found, e.g., in Refs.^[33,34] In contrast to the monolayer case, where the optical transitions between valence band maximum (VBM) and conduction band minimum (CBM) take place around the K point at an energy of ~1.9 eV, in the bulk the momentum-indirect transitions Γ –K and Γ – Λ (Λ is a midpoint between Γ and K) provide the onset of absorption edge at ~1.3 eV.

The change of stacking orders affects both electronic spectra and vibrational properties of layered crystals. The direct observation of valley-dependent out-of-plane spin polarization in 3R MoS₂ was done using spin- and angle-resolved photoemission spectroscopy. This result was ascribed to a non-centrosymmetric structure of 3R crystals, different from the centrosymmetric situation in 2H.^[35] Raman studies demonstrated that interlayer interaction is weaker for the 3R phase, while intralayer vibrational modes are almost identical.^[36] The first principles calculations have shown that symmetry prohibits the splitting of the degenerate states in the bands of bilayer, while this effect appears in the triple layers of MoS₂ with 3R stacking.^[37] In contrast to the 2H stacking, the Γ –K rather than Γ – Λ transitions have the lowest energy in such 3R structures. The stack of three layers can be considered as the onset of “bulk”; thus, such characteristics can be typical for 3R structures (as a preliminary announcement, we emphasize here that this folding can dominate in synthesized NTs).

Most of previous optical studies of the multilayer TMD crystals were done using rather thin samples with a thickness in the 50-500 nm range. These samples were formed by repeated cleaving on an adhesive tape, i.e. by technique which is similar to the exfoliating method currently used. Strong A and B direct band-gap excitonic resonances (two – because VBM is split by the spin-orbit coupling) were observed in absorption spectra of such MoS₂ samples around 1.9 eV.^[28, 38] Similar features in WS₂ are somewhat higher, at ~2 eV. These resonances provide the increase of absorption coefficient up to $1.5 \cdot 10^5 \text{ cm}^{-1}$. The absorption spectra exhibit a shift of about 100 meV when the temperature rises from 77 K to 300 K. Samples with 3R

stacking exhibit the excitonic peaks at slightly lower energies.^[28] The bulk crystals can reflect 20% of impinging light. The optical properties of them are found to be strongly anisotropic. Data on the ordinary and extraordinary refractive indices in MoS₂ can be found, e.g., in Ref. ^[38]. We highlight that no marked optical peculiarities were found in absorption and reflection in the spectral range of weak indirect excitons.

To the best of our knowledge, the first studies of the radiative properties of 2H MoS₂ bulk crystals, both synthesized and natural, were reported much later, in 2003.^[18] PL spectra were measured in the vicinity of indirect excitons. They contain narrow excitonic lines and their phonon replicas in the 1.15-1.3 eV range, as well as a lower-energy broad band centered at 1.0 eV, most likely related to defects. The temperature evolution of the PL spectra revealed the fast quench of the excitonic lines: they almost disappeared at $T > 50$ K. The total PL intensity decreased by two orders of magnitude from 2 K to room temperature. Note that the spectral range of the direct excitons was not investigated during these studies. Thus, the question has been remained whether the direct exciton states are radiative in bulk and multilayered nanostructures.

The discovery of nanocrystal quantum dots in 1980th ^[39] has stimulated the investigation of quantum-size effects in MoS₂ nanocrystals. The synthesized MoS₂ nanoclusters of 2-15 nm in size (3-25 monolayers), suspended in a nonpolar fluid, exhibit distinct spectral features in absorption, which shift towards higher energy with decreasing the cluster size due to the quantum confinement.^[40] The splitting between A and B excitonic peaks increases as well. The lowest energy PL peak in such nanoclusters was registered near 2 eV, which is very close to the energy of direct exciton transitions.^[41] Time-resolved PL (TRPL) measurements in the MoS₂ nanoclusters were performed using a time-correlated single photon counting technique.^[42] It was shown that the radiative recombination is controlled by trap-to-trap relaxation. The emission decay is relatively slow (~200 ps) at 20 K and becomes faster (<40 ps) at room temperature that may evidence an effective carrier transport towards non-radiative centers. Note that the exciton radiative lifetime in a TMD monolayer is very fast, of the order of few picoseconds.^[43]

About ten years later, MoS₂ triangular nanoplatelets of several nanometers in lateral dimensions were fabricated. These particles keep the planar geometry with their size growing; the dangling bonds at their boundaries are stabilized by excess S atoms.^[44] The study by scanning tunneling microscopy (STM) exhibited structural transitions taking place at certain cluster sizes.^[45] Theoretical studies by ab initio calculations have demonstrated in nanoplatelets the possibility of band gap variation in a wide spectral range from indirect to direct excitonic transitions with dependence on the number of sheets and their interspacing.^[46] Such small particles are assumed to be promising for tribology.^[47]

In the common opinion, the PL related to direct excitons should be completely quenched in the TMD bulk crystals and several-layers nanostructures. Indeed, there are experimental data showing a dramatic decrease down to full disappearance of luminescence efficiency in the bulk (several-layers samples) as compared with a monolayer.^[17] It contradicts other studies of flakes comprising a few layers, where both lines of direct and indirect excitonic emission coexist in PL spectra. For instance, to confirm the direct-indirect band gap crossover in MoS₂ Mak *et al.* have measured both direct and indirect exciton lines in samples which contain up to 6 monolayers, i.e. almost “bulk”.^[19] It is interesting to emphasize that the direct exciton line still dominates the PL spectrum in flakes with several monolayers and that its intensity is only one order of magnitude weaker than it is in a direct-gap monolayer. Similar data have been presented by Dhakal *et al.*^[48]

There are several factors that can promote the direct exciton emission in a multilayer structure. Among them is a temperature rise, which can push the system toward the 2D limit by decoupling the neighboring layers with interlayer thermal expansion.^[49] In this case, PL in the multilayer flake exhibits a relatively weak decrease in intensity, by three times only, from 100 K to 400 K. Such robustness might be typical for a monolayer. Elastic strain can affect optical properties similarly (see for review Refs. ^[50,51]). The local strain appears due to either layer extension or curvature; the latter is characteristic for nanotubes. Reduction of the direct band gap and formation of the localization sites was observed on the top of intentionally formed ripples in the monolayers.^[52] Most of the studies of strain effects were done using MoS₂ monolayers.^[53] It was shown that the tensile and compressive strains act in the opposite ways, enhancing either direct or indirect transitions, respectively.^[54] PL spectroscopy demonstrated that the band gap can be tuned in a continuous and reversible way by 500 meV under biaxial strain.^[55] Importantly, it was shown that 2D materials sustain very large deformations without damage. That is why, the strain is currently assumed to be an effective way for the modification of the band structure^[56] and the enhancement of nonlinear optical response.^[57] In both cases, the experimental confirmation was obtained by curving the monolayer samples positioned on a flexible polymer substrate. These results are apparently useful for the consideration of NTs properties.

Recently, there appeared the trend to consider exciton emission dynamics by taking into account momentum forbidden exciton states. It concerns even the TMDC monolayers where the direct gap exciton emission dominates.^[58] Besides, it was recognized that the dynamics is dependent on whether dark or bright excitonic state sit at the lowest energy in a particular material.^[30] It is worth mentioning that the relaxation process of photoexcited carriers in 2D materials strongly depends on the created carrier population and, hence, on the energy of excitation. The closer is the excitation energy to the direct exciton resonance, the more pronounced is its performance.^[48,54,59] Thus, we assume that in a multilayer system there is

always an optimal balance between several competing channels of exciton creation, relaxation, and recombination related to interband transitions between various valleys.

3. Basic optical properties of TMD nanotubes and related curved nanostructures

Electronic band structures of both MoS_2 ^[24] and WS_2 ^[25] NTs have been studied using the density-functional-based tight-binding method. The primary works have considered the nanotubes as a single-wall cylinder constructed by conformal mapping of a triple sheet (X-M-X) with different folding: armchair ($n=m$), zigzag ($n \neq 0, m=0$), and chiral ($n \neq m$). It was found that MoS_2 NTs are mechanically stable. Independently of the folding, all NTs are semiconducting, in contrast to the carbon NTs where the folding type determines either metallic or semiconducting character. The value of a NT band gap rises with increasing the diameter, D , approaching the monolayer limit, because the strain tends to be smaller and smaller with that, following roughly the $1/D^2$ dependence. Experimentally, a confirmation of the band gap dependence on the tube diameter was obtained by scanning tunneling microscopy (STM) measurements of I-R curves.^[60] The particular band-gap character was predicted to depend on the folding type. Namely, the armchair tubes should have a small indirect and a moderate direct gap, while the band gap is direct in the zigzag tubes that, as was suggested. This may be very much promising for light emitting devices. It is interesting to note that this is the first prediction of the direct gap in the monolayer limit, although done for a single-wall MoS_2 NT.

Symmetry-based density functional theory (DFT) calculations of the electronic spectra of single-wall MoS_2 and WS_2 NTs^[61,29] enriched the results of Seifert *et al.* as follows: the direct band gap in a zigzag tube has the same diameter dependence as the indirect band gap in an armchair tube. With increasing the diameter, the indirect and direct gap values in the MoS_2 tube tend to 1.15 and 1.3 eV, respectively. The highest limit for the direct gap of WS_2 NTs is about 1.65 eV. Note that the estimated gap values are markedly lower than experimental ones. For instance, low-temperature absorption spectra peak around 2.1 eV in both WS_2 bulk and the layer comprising arrays of NTs of 15-20 nm in diameter.^[22]

As expected, the curvature-induced strain in the TMD NTs is dependent on the tube diameter: the smaller the diameter the higher the strain. The curvature strain shifts the calculated spectra of optical absorption toward lower energies in unrelaxed MoS_2 NTs, while as a result of strain relaxation the absorption peaks at higher energy.^[62] The concept of the strain influence on optical properties was later developed in a set of papers.^[63-66] The DFT calculations showed that the properties similar to those in monolayer and bulk are realized, respectively, for a large diameter single-wall NT and multiwalled NT. It was predicted that the strain can transform the

direct band gap into an indirect one. Such transition can take place for condition of the tube elongation by as much as of 16%.^[62]

The Raman signals of the in-plane and out-of-plane lattice vibrations should also significantly depend on the strain value. Thus, the Raman spectroscopy is a unique method to determine the strain-dependent characteristics of individual NTs. A review of theoretically evaluated phonon dispersions in the TMD tubes can be found in Ref. ^[29]. The multiwalled WS₂ NTs were investigated by confocal micro-Raman spectroscopy. It was found that the inter-layer vibration mode, A_{1g}, is sensitive to both the curvature-induced strain and diameter, while the in-plane vibration mode, E_{2g}¹, is not affected by them. The competition between the vdW force stiffening and the curvature strain softening provides the shift of the A_{1g} mode frequency by 2.5 cm⁻¹ in the multi-layered nanotubes with small diameters.^[66] The micro-Raman technique was also exploited to establish the relationship between structural and vibrational properties of both nanoplatelets and nanotubes.^[65] It was found that the out-of-plane A_{1g} mode hardens with the increasing number of WS₂ layers, being constrained by the arrangement, while the in-plane vibration E_{2g}¹ mode softens.

Optical absorption and light reflection/scattering in the NTs turn out to be highly anisotropic. In all previous studies, the prevailing signal was polarized along the nanotube axis. This was explained using the formalism of antenna theory, assuming that in a nanotube the depolarization effect strongly suppresses light polarized perpendicular to the nanotube axis. Such effect was investigated by precise Raman measurements of an individual WS₂ nanotube suspended on a cantilever.^[67] The calculated polarized spectra are well consistent with this concept.^[61] We believe that this depolarization effect can concur with the action of optical modes which are polarized along the tube axis as well.^[27] One more interesting feature of NTs is the nonlinear saturation effect (optical limiting) which is stronger than those in the carbon NTs. In the MoS₂ NTs in aqueous suspensions, this effect results in decreasing the transmittance by an order of magnitude with the increasing power of 532-nm and 1064-nm nanosecond laser pulses.^[23]

A set of nanostructures with a curved semicircular surface should be attributed to the family of the tube close relatives. The most interesting example is represented by the nanostructures formed by deposition of a WSe₂ monolayer onto patterned silica substrates with arrays of 150-nm-diameter pillars which have a 60-190 nm height.^[68] The deposited curved monolayer skirts the pillars, forming quantum-dot like localization sites at their tops. These sites, presumably induced by local strain in the 2D material, turn out to be effective quantum light emitters, as it was confirmed by the observation of narrow excitonic lines and single-photon correlation measurements. The narrow lines were recorded in the spectral range of ~50 meV;

thus, a large-scale set of relatively uniform single-photon emitters can be formed using such approach. Another example is the multilayer nanoscrolls produced by rolling up a MoS₂ monolayer within a drop of ethanol.^[21] The direct exciton emission from such nanoscrolls was registered with excitation by a 532-nm laser line. The energy of emission is slightly lower than in a monolayer in agreement with the theoretical prediction of the strain influence.^[61] In this work, the spectral range of indirect exciton transitions was not investigated; thus, there is still uncertainty whether the indirect gap emission exists in such nanoscrolls.

Remarkably, it was reported that WS₂ NTs can sustain both excitonic features and a cavity mode in the visible - near infrared ranges.^[69] This result was obtained using a NT ensemble which represents the aqueous dispersion of 1-10 μ m long NTs of 40 – 150 nm in diameter with 20–40 shells in their walls. The comparison of spectra of the absolute absorption and standard extinction (the later includes both absorption and scattering) have revealed an extra dip arising, presumably, due to the interaction between the excitons and the cavity mode. This observation was supported by performed finite-difference time-domain (FDTD) simulations. The absence of luminescence from the studied NTs was ascribed to the indirect band gap in WS₂. We should note that the direct observation of optical modes modulating the excitonic PL spectrum has been recently (see Ref. ^[27]). This phenomenon will be described in section 7, while in section 6 we present the evidences of PL in multilayered WS₂ NTs.

4. Synthesis of TMD nanotubes

The first reports on the existence of WS₂ and MoS₂ crystals with cylindrical and spherical shapes were published, respectively, by Tenne *et al.* in 1992^[2] and Margulis *et al.* in 1993.^[70] The samples were prepared by sulphurization of the respective metal oxides acted as self-sacrificed precursor crystals, which determined the aspect ratio of the final products. Microtubes and nanotubes of MoS₂ (Figure 1a) and WS₂ (Figure 1b) synthesized by chemical transport reaction (CTR) were firstly reported in 1996^[3] and 1998.^[71] The synthesis of TMD nanotubes by different methods is discussed in a set of comprehensive reviews and books,^[4-7, 2,73] here we focus on the tube formation by the well-developed CTR.

The employed CTR growth mechanism was explained through instability of very thin flakes of layered materials against folding, which triggers formation of rolls from thin flakes or growth of self-terminated tubular structures inside microfolds or bend crystal edges (Figure 1c). The length of the rolls is in a range of a few tens of diameters and they grow only in radial direction in orientation-disordered way. In contrast, the regular stacking between the molecular layers in the tubes enables their growth in longitudinal direction to a length, which extends with duration of a growth process and depends on parameters of the local environment, e. g. on size

and shape of available space, diffusion paths of transported molecules, and vicinity of other tubes or flakes. The growth takes place directly from vapour phase. The tubes grow at a very slow rate and only at their very ends, where the unsaturated bonds represent the nucleation sites with minimal free energy. The adsorbed molecules on the van der Waals surface of a tube are either transported on the surface of the tube along its length, or they are desorbed back to the gas environment. Very homogeneous diameter and wall thickness indicate that nucleation of a next layer on the surface is not preferable and simultaneously evidence an absence of surface defects where such a secondary nucleation would start. How these adsorbed molecules diffuse along the surface of tubes, namely, whether they follow the chirality of the surface atoms, or are hopping to the very end of a tube in straightforward way, is an open question at the time being.

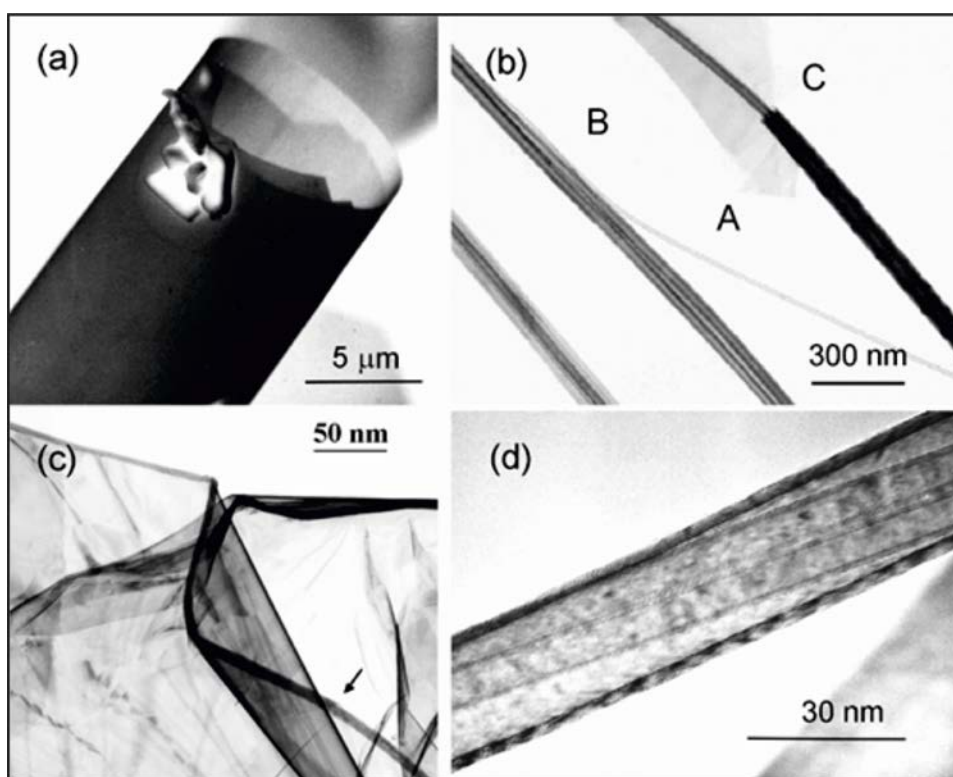


Figure 1. TEM images of different TMD tubes. a) A MoS_2 microtube, 11 μm in diameter and 90 nm in wall thickness; b) WS_2 nanotubes grown as single nanotubes (A), self-assembled into ropes (B) or co-axial nanotubes (C); c) nucleation of a nanotube at the edge of a thin WS_2 crystal; d) two WS_2 nanotubes rolled up around a central nanotube following its chirality.

The MoS_2 and WS_2 nanotubes are synthesized in closed silica ampoules using iodine as a transport agent. During the process of CTR, iodine reacts with the transition metals at high temperature, forming a volatile product, which decomposes at lower temperature, where transition metal reacts again with sulphur, forming solid transition metal disulphide.^[74] The CTR runs from the high temperature zone (1125 K) to the low temperature one (1060 K) with a

temperature gradient of 5.6 K/cm. After three weeks of growth, the silica ampoules are slowly cooled down to room temperature with a controlled cooling rate of 15°/hour.^[3] Approximately a few percent of the starting material is transported in a shape of nanotubes, while the rest of the transported material grows as strongly undulated thin plate-like crystals. The lasting nearly equilibrium growth conditions enable the synthesis of nanotubes of very different sizes, from 10 nm to a few μm in diameter and from a few μm to several hundred microns in length. The tubes always grow together with large area thin flakes, which are typically rotationally disordered about the plane normal. The advantage of this kind of synthesis is an extremely low density of structural defects in the crystal structure of the tubes. It is worthy to mention that CTR mimics crystal growth in nature, where minerals grow in limited space and with limited available resources. Partial pressures of the different elements change during the growth, which affect equilibrium conditions. The nanotubes grow at the end of duration of the growth run and cover the flakes of undulated crystals like spider nets.

While MoS₂ micro and nanotubes usually grow as single tubes, the WS₂ tubes tend to form ropes with the spontaneous self-assembly of the nanotubes during the growth.^[75] Fluctuations of charges and consequent electric attractive forces were proposed as an origin of this attraction. Nucleation of the tubes at edges of thin flakes, inside microfolds and at weakly bond surface steps leads to a nucleation of several nanotubes grown side by side.^[75] A possible nucleation site is also a surface step at the inner or outer surface of a hollow tube, which enables for a growth of more complex tubular structures, like co-axial tubes (Figure 1b), or mutually rolled up nanotubes, where each of the nanotubes follows the lattice structure of the adjacent nanotube^[71] or of the wider central tube (Figure 1d). In the tubular shape of MoS₂ and WS₂, the interlayer distance is extended in average by up to 3% with respect to the 2H_b bulk value.^[3] This extension differs with diameter and number of the layers composing a wall of tube. The extension is the largest near the outer surface, while the separation among the layers shrinks in direction toward the centre of a tube to the bulk value or even to slightly lower value. This leads to mechanical instability in the central layers, which are therefore exposed to breakage.^[5] The reason for this is a strain incorporated in the tubes walls, which is caused by the interlayer stacking and curvature. Although the stacking polytypes were defined for flat geometry, one can speak about the stacking order of the layers in tubular shape too, at least in parts of the tubes. The cylindrical geometry cannot be formed from flat layers without consideration of strain in extended and contracted triple S-Mo-S or S-W-S layers, and/or creation of defects, which relax this strain, when it exceeds a critical value.

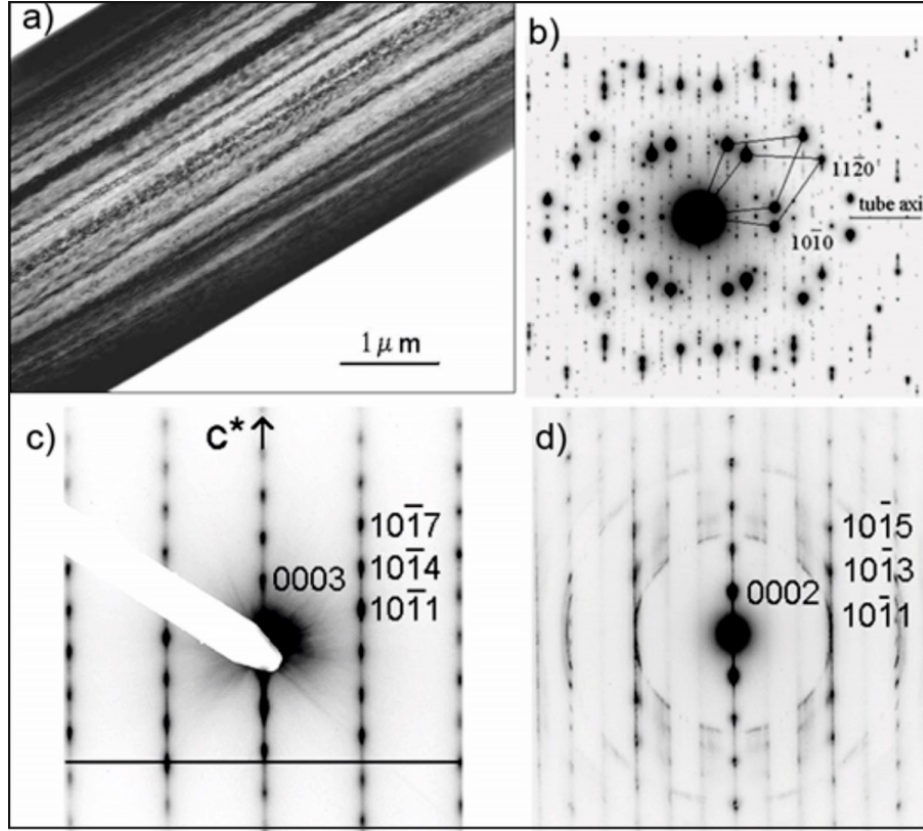


Figure 2. a) MoS_2 microtubes with bending contours along the MoS_2 microtube axis revealing strips of semi-long-range order, satisfying Bragg's condition for electron scattering. Electron diffraction patterns taken: (b) at the central part of the tube as a superposition of electron scattered by upper and lower walls revealing the chiral growth mode; (c) at the tube edge with the rhombohedral 3R stacking sequence in accordance with the rule $(-h+k+l=3n)$; (d) on a nanotube, 190 nm in diameter, crystallized in the $2H_b$ stacking sequence satisfying the rule $l=\pm(2n+1)$.

The tubes grow in chiral growth mode with angle of chirality between projection of the tube axis on [0001] basal plane and the $\langle 10\bar{1}0 \rangle$ lattice direction (Figure 2a,b). Microtubes with diameters around a few μm grow in orthorhombic (3R) stacking (Figure 2c), while more narrow nanotubes are crystallized in hexagonal ($2H_b$) stacking (Figure 2d).^[76] This difference influences the optical properties of the nanotubes due to in-built lattice strain in the microtubes, which causes up-shift of Raman peaks with respect to the bulk.^[77] The lattice parameters in bulk 3R polytypes are for approx. 1% (MoS_2) and 2 % (WS_2) larger in basal plane, and slightly (0.2 %) shorter perpendicularly to the layers.^[28] In microtubes, the strain is distributed over a larger number of primitive unit cells composing the circumference of a tube and stabilizes a high-pressure 3R stacking, which is in bulk stable at pressures above 40 kbar.^[75] The strain intensity is increasing toward the central part of a tube that stabilizes the coexistence of several diameters over the whole length of a tube. As grown tubes are open ended, but not all of ideal cylindrical shape. If a tube meets an obstacle during the longitudinal growth, it deforms to elliptical cross

section or collapses to the shape of a ribbon, and then continues its growth in this new shape. Because of the chiral lattice structure, the strain at strongly bend molecular layers at longitudinal edges of the elliptical tubes or ribbons causes spiral twisting of these forms.^[78]

5. Experimental details and samples characterization

To investigate the optical properties of individual MoS_2 and WS_2 NTs we used two setups for micro-spectroscopy measurements, which have different functionality. Both setups exploited an optical confocal scheme. They are equipped with a silicon liquid nitrogen cooled CCD for the mPL measurements in the visible – near infrared range (up to 900 nm). Micro-cryostats allowed the measurements at different temperatures down to 8 K. Large working distance lenses (Mitutoyo 100×NIR, NA = 0.50) and pinholes ensured the light collection from a $\sim 2\text{-}\mu\text{m}$ spot on a sample that enables to measure mPL from a single tube.

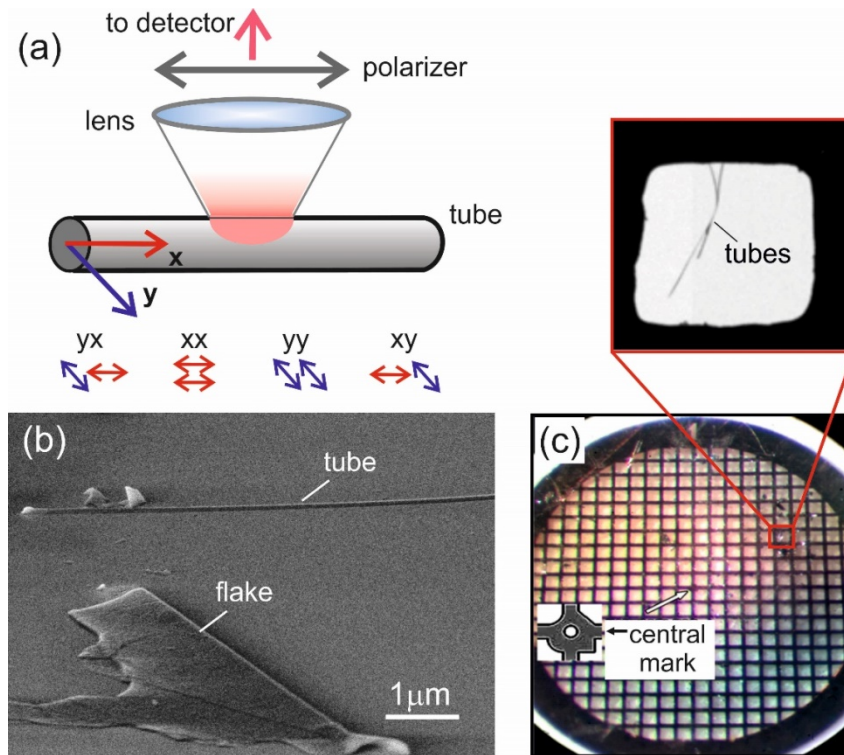


Figure 3. (a) Schematic of the excitation and detection of mPL from a single nanotube. Red and blue arrows in bottom indicate possible polarization configurations with respect to the tube axes. The notation used like “yx” reads as follows: excitation along the “y” axis, detection along the “x” axis. (b) SEM image of a nanotube and a flake on a silica substrate. (c) Square mesh TEM grid of ~ 2 mm in diameter with suspended tubes, ribbons, and flakes used in the experiments. The inset shows one cell with the higher magnification. The asymmetric central mark is useful to find a cell.

One of these setups is equipped with piezo-drivers Attocube XYZ placed inside the helium cryostat that allowed us to set and hold the position of selected nanotubes during quite a

long time. In particular, it is possible to measure the mPL spectra emitted from different points along a tube offering us the possibility to estimate its homogeneity. Besides a CCD, this setup also involves a silicon avalanche photodiode operated in a time-correlated single photon counting mode that permit us to measure mPL with a temporal resolution of about 45 ps. The TRPL measurements of tubes and flakes were done at low temperatures (10 K) using for excitation a 404-nm (3.07 eV) picosecond pulsed semiconductor laser. Power of the laser was 1 mW in average, measured in front of the cryostat window. The repetition frequency of the pulses was 100 MHz. To detect PL decay curves at selected wavelengths the collected emission was dispersed by a grating monochromator.

The other setup was primarily intended for micro-Raman (mR) spectroscopy. The Raman spectra were always measured to characterize quality of the studied samples. Besides, the intensity of Raman scattering was registered during the scans of PL bands that was used afterwards for normalization of the PL intensity as described in Ref. ^[17]. In this setup, the linear-polarization sensitive measurements of mPL were done in four possible configurations (see Figure 3a). This setup comprised a Horiba Jobin-Yvon T64000 spectrometer equipped with a confocal microscope and a silicon CCD. A temperature controlled microscope stage Linkam THMS600 allowed realization of temperature-dependent measurements. In addition to the CCD, the setup possessed an InGaAs-based linear diode array (sensitivity range 0.8–1.7 μm). Combination of two detectors allowed us to determine the true shape of indirect exciton emission, which is located spectrally just at the sensitivity boundaries of both. Besides, it enables to control the defect-related emission which might appear at ~ 1 eV. ^[18] In these continuous wave (CW) measurements, we used a 600 gr/mm grating and a 532 nm (2.33 eV) line of a Nd:YAG laser for excitation.

We have investigated both tubes and flakes grown in the same silica ampoule during the same growth run of CTR, as described in section 4. For reference, the flakes exfoliated from a commercially available high-quality MoS_2 bulk crystal (“HQ-graphene” production) were studied as well. Besides the conventional samples on a SiO_2/Si substrate (Figure 1b), we have studied the free-standing tubes and flakes, which were suspended in a square mesh TEM grid commonly used for TEM investigations (Figure 1c). We have previously exploited this approach to establish the link between mPL and structural defects in a quantum well structure. ^[79] Importantly, the use of free-standing samples excluded the possible effect of a substrate. ^[80-82] Besides, it permitted us to perform the TEM characterization of selected tubes to obtain additional data on structural properties. It is worth mentioning that no strong difference in PL spectra was found between the samples mounted by different ways; we rather observed the strong difference between the tubes and flakes.

Before the mPL studies, the samples were characterized by micro-Raman spectroscopy. The typical room-temperature Raman spectra of NTs and multilayer “bulk” flakes are presented in Figure 4. The polarization dependency of the Raman active modes, with almost full suppression of A_{1g} in the yx polarization, evidences the good structural quality of CTR NTs. Complimentary studies of exfoliated flakes of atomic thicknesses gave us the mode-energy-thickness dependence which is described in literature.^[83] The measured shifts of the E_{2g}^1 and the A_{1g} modes with respect to their positions in a monolayer, indicated in Figure 4b, correspond to the “bulk” case, when the number of monolayers is definitely more than ten. In the low-frequency range, the shear mode at 32.5 cm^{-1} is significantly suppressed in the tubes, as can be anticipated.^[84] Thus, we confirm that all our tubes under study are multiwalled. The increase of the A_{1g}/E_{2g}^1 intensity ratio, along with the appearance of some contribution of a breathing mode at the low-frequency side of the shear peak, is suggestive of the 3R folding.^[36] These findings are well consistent with previous TEM studies revealing the dominance of the 3R polytype in the relatively large multiwalled tubes grown by CTR (see section 4).

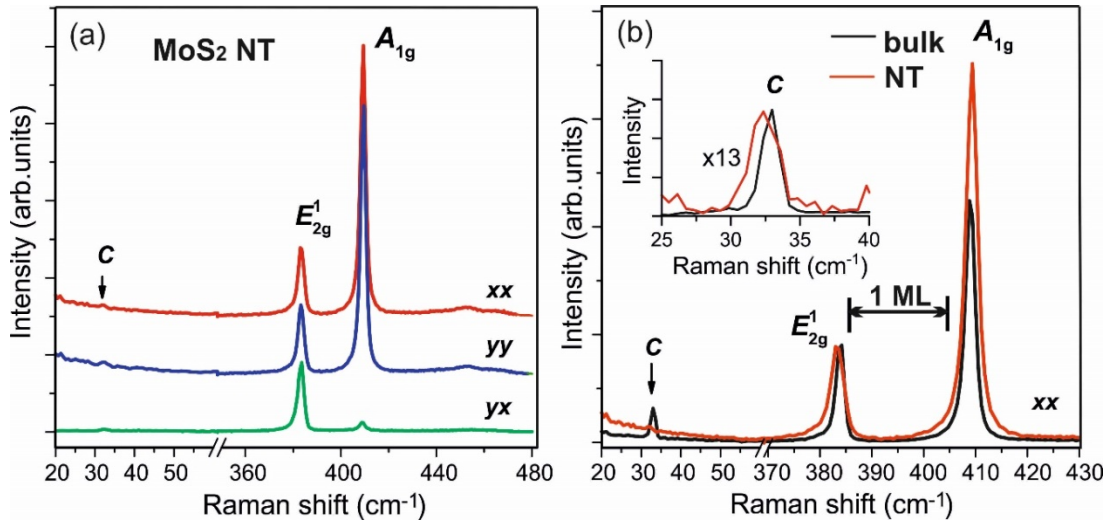


Figure 4: Raman spectra of a MoS₂ tube of 2 μm in diameter measured at room temperature using a 532-nm line excitation: (a) spectra taken in different polarization configurations marked in the plot; (b) comparison of Raman spectra measured in the tube and in a multilayered “bulk” flake. The inset shows the range of low-frequency modes.

6. Luminescence emerging from TMD nanotubes

We studied micro- and nanotubes of different diameters ranged from 400 nm to 2 μm and found that they are radiative. Characteristic low-temperature spectra of MoS₂ and WS₂ NTs recorded in the spectral range of direct excitons are displayed in Figure 5. Amazing fact is the observation of bright direct exciton emission from the multilayered structures, which are expected to possess an indirect band gap. Moreover, the integral PL intensity in the MoS₂ NTs

appears to be an order of magnitude higher than in the flakes made during the same growth run. This estimation is done taking into account the ratio of excited surface areas, S , i.e. $sS_{\text{flake}}/S_{\text{tube}} \sim 5-10$. The intensity of emission from the WS_2 tubes is markedly lower, probably because of the non-ideality of the WS_2 NTs, described in section 3. However, they resemble the MoS_2 tubes in many aspects such as the temperature behavior of PL and the performance of resonant optical modes (see section 7). This permits us to present here the results obtained using more stable and brighter MoS_2 NTs, which can be considered as a typical representative of the TMD tube family.

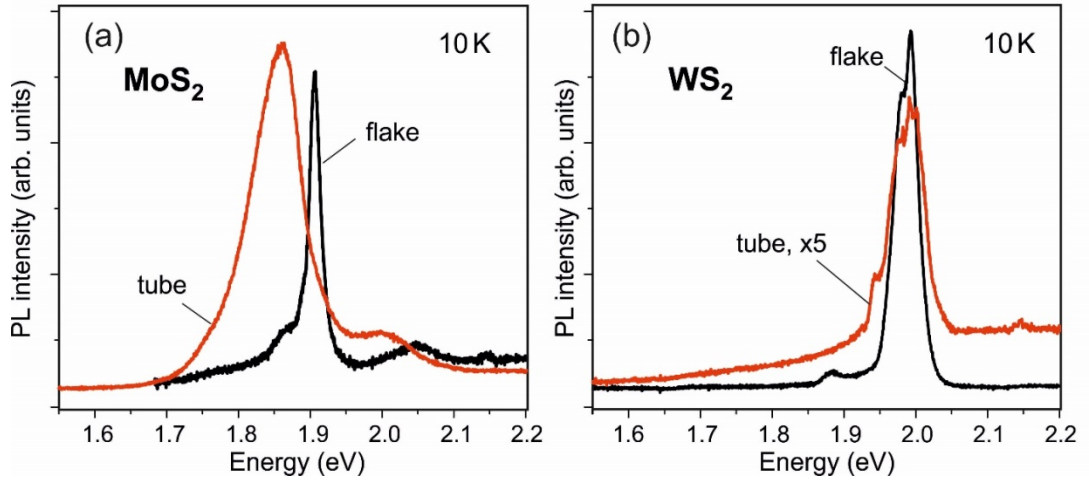


Figure 5. Spectra of mPL measured in the spectral range of direct exciton transitions at 10 K from (a) MoS_2 and (b) WS_2 nanotubes with the diameters of $\sim 0.4 \mu\text{m}$. Excitation was done with a 404-nm laser line. The non-ideality of the WS_2 tube results in the lower PL intensity, while in the perfect MoS_2 tube the integral intensity can significantly exceed the one in the flake.

At low temperature, the spectra of the MoS_2 NTs display peaks at 1.86 eV and 2.00 eV, related to A and B excitons, respectively. Their energies are close to those in planar atomic layers.^[18] The red shift of the peaks by ~ 50 meV with respect to the emission from the flakes can result from the combined actions of unrelaxed strain in the tubular structures^[61] and 3R folding type (the excitonic peaks are red-shifted in 3R bulk MoS_2).^[28] In contrast to the PL from bulk crystals, which quenches completely at temperatures above 50 K,^[18] the emission from the CTR NTs exists up to room temperature.

The common feature of MoS_2 tubes and flakes is rather weak emission at low temperature of a phonon-assisted indirect exciton, while the direct exciton related emission is very pronounced. Among obvious reasons for that, we should mention the low population of the phonon bath at helium temperatures and the possible decoupling of neighboring layers.^[49] With increased temperature, one can observe two bands of direct and indirect excitons in the PL

spectra of both tubes and flakes (Figure 6). However, their dependencies with the temperature rise are different. The intensity of the direct-exciton PL drops with rising the temperature in both cases, as it takes place in conventional semiconductors, whereas the PL intensity related to the indirect exciton transitions increases. Moreover, the increase of the indirect-exciton PL in NTs is very weak as compared to the planar flakes. A still unknown fine structure of the excitonic states in the NTs can be responsible for such distinctive feature.

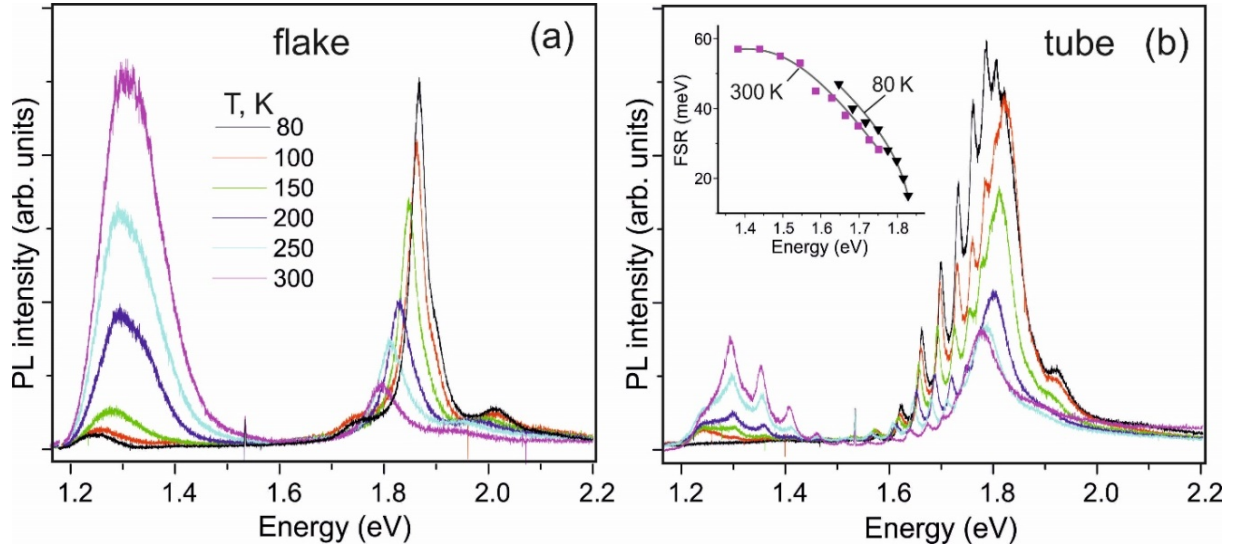


Figure 6. Temperature variation of mPL spectra in MoS_2 structures: (a) flake and (b) tube with $2\ \mu\text{m}$ in diameter. The sharp peaks of WGMs modulate the spectra. The inset shows the energy dependence of free spectral range (FSR) between adjusting peaks, which follows the refractive index variation with temperature.

The characteristics of PL decay in the NTs resemble those of the radiative process in monolayers^[85] rather than in bulk. The basic decay of the direct-exciton PL, measured at low temperature (Figure 7), turns out to be fast in both tubes and flakes. Its characteristic decay time is less than the temporal resolution of our system ($<45\ \text{ps}$). A slowly decaying PL component, related presumably to localized states, decays almost similar in both tubes and flakes with decay time constant $250\ \text{ps}$ and $280\ \text{ps}$, respectively. We notice that the fast PL component in the NT decreases more rapidly and falls to the smaller value than in the flake, which likely evidences more effective recombination process of the direct band gap excitonic transitions in the NTs. This assumption is consistent with the mPL spectra measured in a wide spectral range, which demonstrate relative suppression of indirect exciton emission in the NTs (Figure 6).

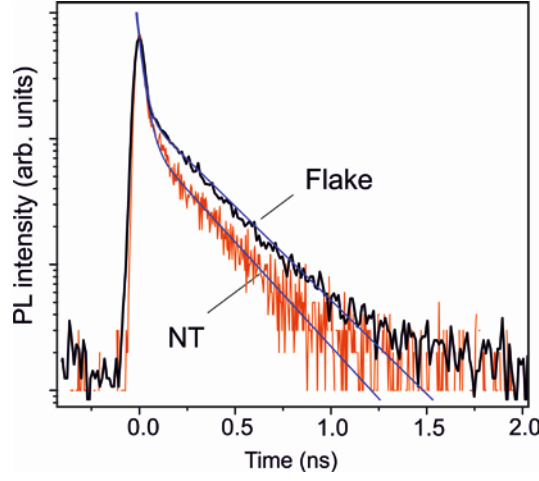


Figure 7. PL decay curves measured at 10 K at the direct band-gap exciton peak energy in a MoS₂ nanotube of 500 nm in diameter (red line) and in a flake (black line). The solid lines show two-exponential fittings.

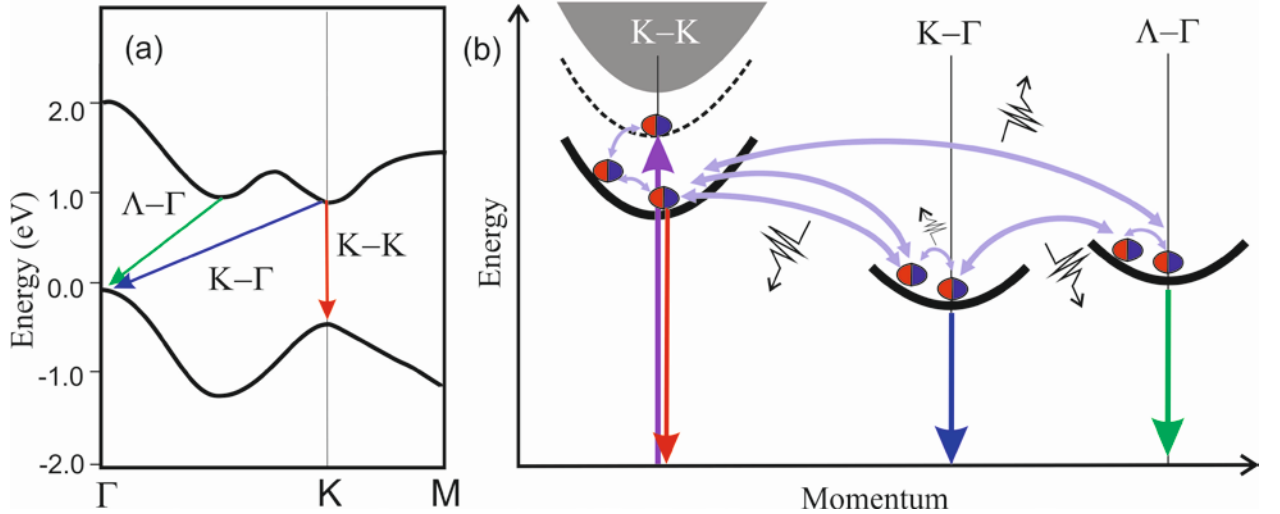


Figure 8. (a) Schematic band structure of multilayered 3R MoS₂ where only the lowest conduction and highest valence bands are depicted. (b) The scheme of formation, relaxation, and radiative recombination of momentum direct (K-K) and indirect (K-Γ and Λ-Γ) excitonic states (red, blue, and green arrows, respectively) with quasi-resonant excitation. Fractured arrows depict absorption/emission of phonons.

By globally considering these findings, we underline that the direct and indirect exciton recombination channels cannot be considered separately in the multilayered tubes and flakes. To clarify that, we present in Figure 8 the sketch of the 3R-politype band structure together with the scheme of exciton creation, relaxation and recombination. Obviously, when the recombination rate of strong direct excitonic resonances is high enough, the K-K transitions can recombine with emitting a photon instead of transferring the excitations towards the K-Γ or Λ-Γ states by a less probable phonon-assisted mechanism. As described in section 2, there are several factors that can promote the direct exciton emission in multi-layered systems. In particular, using a

quasi-resonant excitation and strain characteristics for the NTs can change the ratio between the direct and indirect excitonic transitions. We cannot also ignore such effects as interlayer coupling and exciton tunneling in chiral structures.^[86, 87]

7. TMD tubes as optical resonators

The tubular microcavities supporting whispering gallery modes (WGMs) have attracted much attention due to their unique properties, such as subwavelength dimension, light polarization, and superior optical confinement due to the absence of higher-order radial modes. That makes them promising for different nanophotonics applications, including lasing.^[88, 89] A variety of techniques were exploited to fabricate tubular resonators from “epitaxial casting”, when in a core-shell column structure the core is etched, to direct lithography formation.^[90, 91] The rolling-up strained thin films or membranes were also used to form tubular microresonators.^[92] The high quality of such rolls provides spectra with sharp peaks of optical modes.^[93] A specially designed bottle-like shape with varied numbers of layers in a wall allowed ones to study relevant effects of light confinement, mode splitting and chirality.^[94-96] We should underline that the studies of the microtubes and microrolls as optical resonators have mainly concerned the tubular structures made from layers of bulk materials. In the 2D family, the carbon nanotubes have solely been investigated as a part of optomechanical and hybrid cavity systems.^[97-99] To the best of our knowledge, the first demonstration of a single synthesized NT acting as a resonator has been done during our studies^[27].

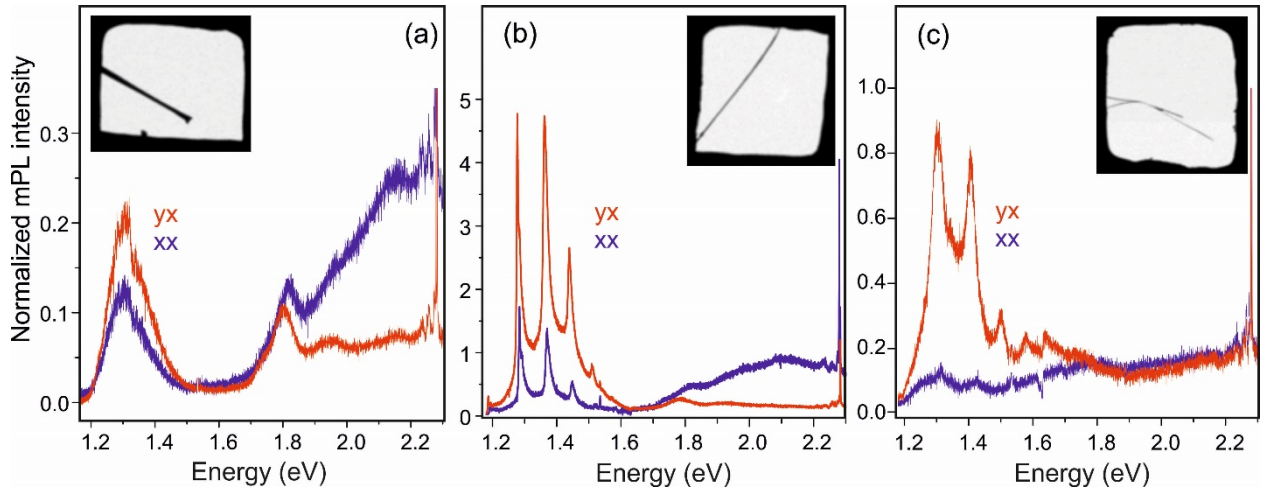


Figure 9. *mPL spectra normalized to phonon mode intensity of samples suspended in a mesh cup as shown in the inserts: (a) 4- μm -thick ribbon; (b,c) two tubes with the diameters 2 μm (b) and 800 nm (c). The spectra are registered at room temperature in two different polarization configurations using a 532-nm laser line with 0.4-mW excitation power. The difference between higher-energy parts of the spectra is mainly due to the different light scattering along and across the tube/ribbon axes. No sharp peaks are observed in the spectra of the ribbon.*

The typical mPL spectrum with pronounced sharp peaks related to the optical modes is shown in Figure 6b. The energy dependence of the energy splitting between adjacent peaks – free spectral range (FSR) – and its temperature shift follow the refractive index variation near the A exciton resonance, as it was observed previously for the WGMs in a cup-shaped resonator.^[100] We found that the WGM peaks are strongly polarized along the tube axis. This effect was observed in the NTs of various diameters placed both on the silica substrate and suspended on the TEM grid (Figure 9). It is worth noting that the WGM peaks, emerging at the same energy, are strong in the yx and xx configurations. They are suppressed in two other, xy and yy, configurations. That is why we present here the spectra only for the strongly different yx and xy configurations. To compare the PL intensity in different samples we normalize in Figure 9 each PL spectrum to the intensity of the phonon mode E_{2g}^1 , not dependent on layer thickness and polarization (see Figure 4a). This normalization excludes a possible difference in excitation power densities due to accidental tube displacement and reasonably reflects the PL efficiency.^[17]

The WGMs peaks are not observed in the collapsed tubes – ribbons (Figure 9a). Thus, their observation is a way to distinguish the tubes from the ribbons. In the spectra of NTs with small diameters (<500 nm), the WGM related peaks are absent (see, as an example, the spectrum of a 400-nm tube in Fig 5a). On the contrary, in tubes of large diameters $\sim 2 \mu\text{m}$ the WGM peaks are very pronounced and the quality factor $Q=\lambda/\Delta\lambda$ of the tubular resonator can be as high as 100-200 (Figure 9b). As a result, the PL intensity at the WGM frequencies can be locally increased by 50 times. Consideration of the spectra presented in Figure 6b and Figure 9 shows that the optical modes can enhance any of the band of two, related to direct or indirect excitons. Obviously, the spectral position of the WGMs must depend on the tube diameter and the wall thickness in a tubular resonator.

The theoretical consideration of optical modes quantified in the walls of vdW NTs can be found in our recent paper.^[27] Briefly, the mPL spectra of NTs were modelled for different polarization configurations using the Lorentz reciprocity theorem. After excitation by $E(\omega)_{\text{exc}}$ at the frequency ω , the exciton generation in the wall at a radius r from the tube center and at an angle θ is characterized by the spatial distribution $P(r\theta)$. Electric fields induced along orthogonal directions E_θ and E_x determine the PL spectra in two experimental configurations $\text{PL}_{xy}(\omega)$ and $\text{PL}_{yx}(\omega)$, respectively. The exciton generation is followed by rapid energy relaxation to the recombining states. The subsequent photon emitting occurs with the conservation of real space distribution and the loss of polarization. The non-polarized PL is modulated by the strongly polarized resonator modes. We achieve the perfect modelling the energy and shape of the WGM peaks assuming one monolayer fluctuation in the wall thickness. Since the number of

monolayers, N , in the tube wall is the fitting parameter; the modelling is used to estimate this quantity. In particular, $N \approx 45$ is derived for the microtube whose spectra are shown in Figure 6b.

The WGMs have zero wave vector along the NT axis and oscillate in the azimuthal direction with frequency which is dependent on the azimuthal angular momentum number, m , which in turn depends on the tube diameter, D , and N . The difference between yx -polarized and xy -polarized PL, which is clearly seen in all measured spectra, is explained by the different angular momentum numbers m of the modes supported at certain energy in these polarizations. It is well known that the Q-factor increases with the rise of m number.^[101] Our modelling has shown that near the A exciton, the m value is about 20 in the yx polarization, but it is significantly less in the xy polarization. As a result, the PL intensity in the peak increases until the strong absorption at the direct exciton resonance disables any enhancement.

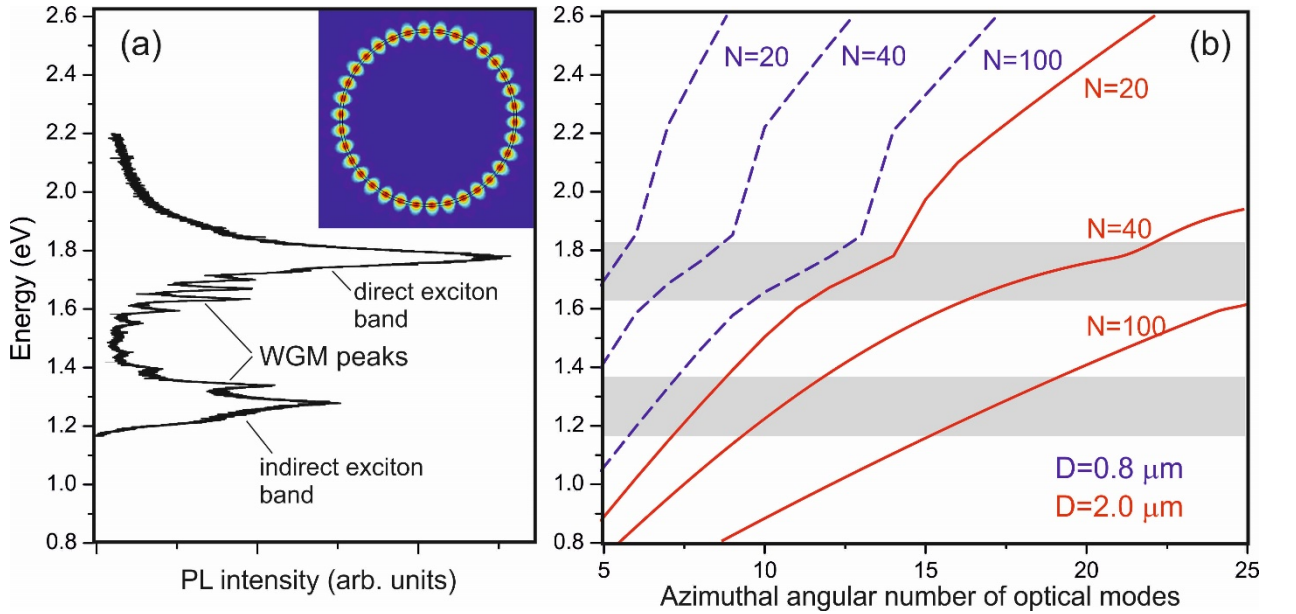


Figure 10. (a) Typical PL spectrum measured in a MoS_2 tube with the diameter $D=2 \mu\text{m}$ and an estimated number of monolayers $N \approx 45$. The WGM peaks are pronounced below the direct exciton resonance. The inset represents the electric field distribution in the tube wall for the x -polarized WGM with azimuthal angular number $m = 20$. (b) Dependences of the optical mode energies on m calculated for the tubes with $0.8 \mu\text{m}$ (blue lines) and $2 \mu\text{m}$ (red lines) diameters and different number of monolayers in their walls, N , marked in the plot. Shaded areas denote the spectral ranges of excitonic emission.

In general, to provide a reasonable enhancement an essential part of the mode energy should be confined inside the tube walls that is also achieved with $m \geq 20$. To illustrate that, we show in Figure 10a the characteristic NT spectrum with the WGM peaks plotted along the vertical axis. The inset in this figure shows the confined energy distribution. Figure 10b presents the dependences of the mode energy on m , calculated for two diameters (0.8 and $2 \mu\text{m}$) and

different N (20, 40, and 100). This plot demonstrates that the larger N , the more slopping is the dependence at the same tube radius, while the thinner is the tube wall (small N) the higher is the energy of the supported mode. Comparison of two panels (a) and (b) shows that in order to enhance the emission of direct exciton band at 1.9 eV the tubes must be of large diameter and relatively thin-walled. This is realized for the $\sim 2\text{-}\mu\text{m}$ tube with $N\sim 40\text{-}50$. The optical modes in the thick-walled tubes of large diameters (almost full cylinder) can enhance only the indirect exciton PL near 1.3 eV (Figure 9b), whereas the MoS_2 tubes supporting the modes with $m < 15$ can provide a rather moderate enhancement but at higher energy. The experimental spectra measured in micro- and nanotubes are well consistent with this simplified consideration.

8. Conclusions and future outlook

In summary, we present optically-active TMD micro- and nanotubes synthesized by well-developed CTR technique which ensured their excellent structural properties. Our data show that the multilayered tubes are both radiating and resonating. Moreover, they exhibit emission not only related to the indirect excitons but also to direct ones, and it is found that the later can dominate the emission spectra. In the common opinion, any multiwalled structures made from indirect-band gap TMDs cannot effectively radiate; their emission is expected to be weak and hardly measurable. To clarify the failure of this opinion with respect to the NTs, we have reviewed old and recent studies on electronic band structures and optical properties of bulk TMDs and related nanostructures, including curved and tubular ones. It has been found that several factors can promote the unexpected performance of excitonic emission. Among them, there are strain, interlayer distance variation, and quasi-resonant excitation. In addition, there should be some peculiar factors such as internal tubular arrangement – specific folding and chirality, as well as the fine structure of excitonic states, comprising both bright and dark excitons. Full understanding of the role of these factors requires thorough additional investigations. We believe that micro-spectroscopy with temporal resolution and with applied magnetic field, supported by theoretical considerations, can shed light on the unusual optical properties of the TMD NTs.

Concerning the resonating ability of TMD NTs, we should underline that the spectra with strong WGM peaks were measured at room temperature and that the Q factor as high as several hundred is achievable in the synthesized MoS_2 tubes. This opens a way for their applications as effective microresonators in nanophotonics. Note that the manipulation by these tubes does not require the laborious "tape" technology (we produce our samples using conventional tweezers) and their surface remains clear after the manipulations, without any contaminations. The smallest tubes can be readily transferred using some liquids. These advantages and exceptional optical

properties present a playground for realization of interesting nanophotonic systems where the NTs can be used for reemitting, selective enhancement, and transferring of the electromagnetic energy.

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