*Semiconductor Physics, Quantum Electronics & Optoelectronics, 2025. V. 28, No 1. P. 037-046.*

*Hetero- and low-dimensional structures*

# Two-dimensional $MoS_2$ for photonic applications

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**Abstract.** Two-dimensional molybdenum disulfide ($MoS_2$) has garnered significant interest in optoelectronics due to its direct band gap, tunable optical properties and the potential for realizing the van der Waals heterostructures. This article provides a comprehensive overview of 2D $MoS_2$ and its applications in photonics. We begin by discussing recent advancements in the bottom-up synthesis of $MoS_2$ using chemical vapor deposition, focusing on novel approaches using liquid molybdenum precursors. Then, we review the latest developments in light-based devices leveraging $MoS_2$, including light-emitting diodes, photodetectors, waveguides, optical cavities and single-photon sources. By summarizing recent achievements, this review provides insights into the prospects offered by $MoS_2$ in photonics.

**Keywords**: photonics, 2D materials, molybdenum disulfide, chemical vapor deposition, liquid precursor.

https://doi.org/10.15407/spqeo28.01.037
PACS 42.70.Qs, 77.84.Bw, 81.15.-z

Manuscript received 16.08.24; revised version received 12.09.24; accepted for publication 12.03.25; published online 26.03.25.

## 1. Introduction

Photonics refers to the phenomena in which light, instead of electrons, is used to transmit or process information: it has played a crucial role in recent advancements in technology and developments in different fields, namely telecommunications, healthcare and energy, with widely studied and continuously optimized applications, namely lasers, Bragg gratings, waveguides, ring resonators, optical modulators and photodetectors [1, 2]. Several classes of materials and compounds have reached commercial exploitation and are currently used in photonics applications. However, these materials usually combine specific advantages with several drawbacks. Silicon, for example, as a well-known material with its robust technology, has an indirect band gap that limits light emission and absorption efficiency, especially within the visible range. Its centrosymmetric crystal structure inhibits second-order nonlinear optical interactions and the difficulty of monolithic integration in the mid-infrared range. III-V compounds, namely GaAs, GaP, InP, AlGaAs, InGaP, and GaN have direct band gaps and efficient light emission and absorption. However, they are more expensive and exhibit limitations within the infrared range. Additionally, in the case of GaN, there is a lack of cheap native substrates. Photonic crystals can conveniently manipulate light propagation and are used to create novel optical devices. However, they have limited operating band width, difficulties in fabrication, and are very sensitive to structural imperfections [3]. The necessity to integrate different technologies and functionalities in a single chip, the gradual approaching of fundamental limits of current materials, the need for optimized devices, reduced production costs and the evolving market demands cause the research of novel solutions to overcome the limitations of current technologies. Thus, it is imperative to explore new materials, understand fundamental phenomena and create new building blocks for innovative photonic devices.

Since the discovery of graphene, many materials have been thinned down to single or few stacked layers and have shown properties completely different from their bulk counterparts. The vertical dimension plays a significant role in determining material properties since the interactions between various layers, governed by van der Waals forces, are much weaker than the forces that drive the in-plane electrons.

Besides graphene, two-dimensional (2D) materials, namely transition-metal dichalcogenides (TMD) [4], black phosphorus/arsenic [5], and boron nitride [6] have opened up new frontiers in material science and engineering, which is caused by their unique optical, electronic, and spin properties that can significantly enhance light-matter interaction, improve speed and sensitivity, potentially reducing the footprint and power consumption of optical devices. Various 2D materials can also be stacked one on top of the other to implement the so-called “van der Waals heterostructures”, which virtually eliminate the lattice mismatch problems, allowing investigations of unusual properties and new phenomena and further expanding the possibilities of these systems. Even more interesting is the possibility of integration with already developed photonic structures to create new hybrid devices that can combine the best properties of different classes of materials [7].

Amongst 2D materials, molybdenum disulfide ($MoS_2$) has a lot of attention due to its easy synthesis and convenient physical properties. In particular, the band gap of $MoS_2$ switches from indirect to direct when thinned down to the size of the monolayer, resulting in a significant enhancement in light emission and optical absorption. Monolayers of $MoS_2$ show a significant photoluminescence, which can be exploited in photonics and optoelectronics applications [8]. Despite its atomically thin nature which somewhat limits the light-matter interaction, resulting in low absorption within the range 450–700 nm, $MoS_2$ was proved to be suitable as an active material in devices, namely light emitters and photodetectors. Resonant photonic structures were proposed to overcome these intrinsic limitations [9]. $MoS_2$ has two types of excitons: propagating excitons which can resonate with incident photons due to their large oscillation strength, and excitons tightly bound to defects, which can act as single-photon emitters. The planar exciton confinement effect can also enhance light-matter interaction. The combination of plasmonic nanostructures and $MoS_2$ also demonstrates the enhancement in light-matter interaction, allowing potential applications in nanophotonic devices [10]. Despite all the progress, the achievement of a high quantum yield in $MoS_2$ is still a challenge [11]. A lot of work has already been done in this field, and many research papers on the investigation of 2D materials for photonic applications have already been published, including several general reviews to which the reader is addressed. Hence, in this review article, we are focusing on the specific and more recent results concerning only 2D-$MoS_2$ and its various applications in the photonics field, where research is extremely active and various device structures have been proposed. There are excellent reviews dedicated to $MoS_2$, but they either cover all aspects of the material without an in-depth analysis of photonic devices [12, 13] or discuss only photodetectors [14, 15] without considering other possible applications in the realm of light-based devices.

Therefore, we aim to fill a gap that can be useful for both researchers focused on these unique materials and scientists interested in different types of photonic devices by giving some new insights concerning the most recent results in the preparation of 2D-$MoS_2$ by chemical vapor deposition (CVD) and by reviewing a different type of photonic devices based on this material.

## 2. Preparation of 2D-$MoS_2$

### 2.1. Synthesis by chemical vapor deposition

CVD offers a combination of low cost, uniformity, scalability and reproducibility of TMD synthesis [16]. CVD involves the reaction of precursor gases on a heated substrate with precise control over the thickness and quality of the $MoS_2$ layers. Many excellent reviews on the CVD growth of 2D materials are available in the literature for the reader interested in the details of this method [17, 18]. Hence, we will limit our discussion to the most recent relevant results, in particular regarding the use of liquid precursors.

Recently, Zhang *et al.* [19] built a miniaturized CVD system capable of observing and recording the real-time growth of 2D-$MoS_2$ crystals. Image processing techniques convert real-time footage into digital data, and machine-learning algorithms are employed to unveil the significant factors influencing the growth of $MoS_2$ crystals. The model successfully predicts CVD growth parameters for the synthesis of ultra-large monolayer $MoS_2$ crystals and demonstrates the potential for reverse engineering the growth parameters by analyzing the as-grown crystal morphology. In the synthesis of 2D-$MoS_2$ using CVD, liquid-precursors-intermediated synthesis (LPI-CVD) overcomes the challenge of unstable nucleation that arises from the difficulty in controlling the evaporation of solid precursors [20], by facilitating their transport and reaction in the gas phase. Liquid precursors can be more homogeneously mixed with carrier gas, resulting in a more uniform material. In addition, liquid precursors allow for precise control over the composition and concentration of precursor species, enabling the tuning of TMD properties, namely thickness, crystallinity and doping levels. These precursors offer advantages, namely good solubility, higher vapor pressures, high volatility and controlled decomposition under appropriate conditions, which are essential for the controlled growth of high-quality $MoS_2$ films. Some of the most used molybdenum compounds include $(NH_4)_2MoS_4$ [21], $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ [22, 23], $Na_2MoO_4\cdot 2H_2O$ [24], and $MoO_3$, which, unlike the first three, is not soluble in water but in $NH_4OH$ [25]. These components are then dissolved in a specific solvent and spin-coated on a substrate. The solution concentration, the spinning speed and the spin time are carefully controlled to achieve the desired film thickness and uniformity. After spin-coating, the precursor-coated substrate is typically annealed in a furnace under controlled temperature and atmosphere conditions. This annealing step converts the precursor film into molybdenum oxide or another intermediate phase, which is subsequently sulfurized and converted into $MoS_2$. SCVD/LPI-CVD method enables direct reaction and nucleation on a substrate.

Plasma cleaning is often employed as a pre-treatment step before the growth, particularly when liquid precursors are used, for the following reasons. (i) Surface cleaning: plasma cleaning effectively removes organic residues, contaminants and surface oxides. (ii) Improved adhesion: plasma treatment can improve the adhesion of

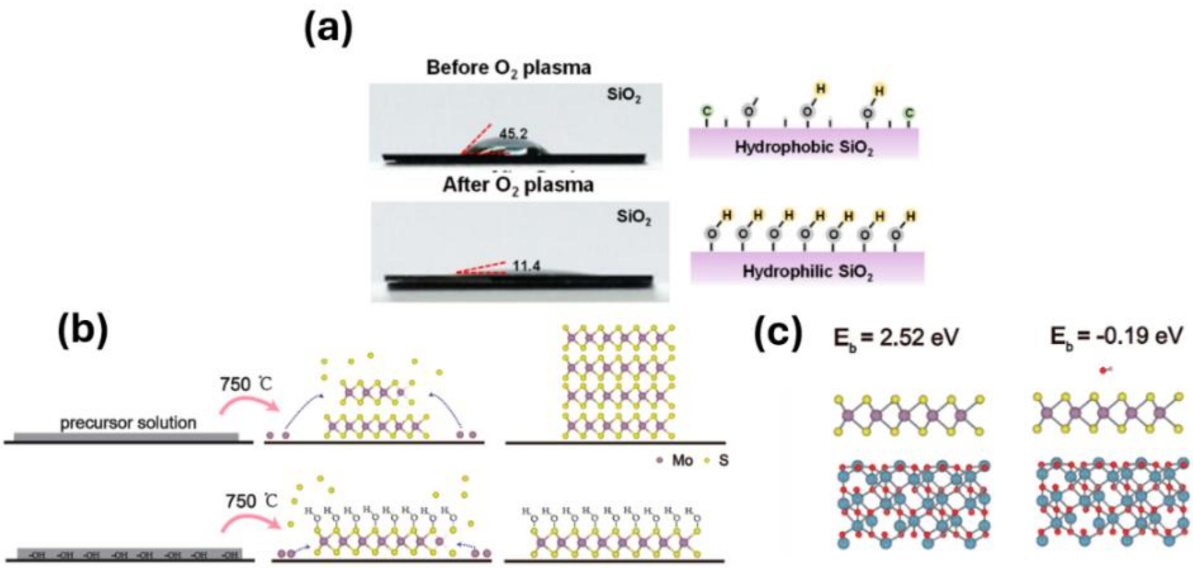


**Fig. 1.** (a) Plasma cleaning treatment of the surface before the CVD growth. Reprinted with permission from Ref. [26]. Copyright 2021 American Chemical Society. (b) Difference between the vertical growth in the absence of the −OH groups (up) and the lateral growth enhancement in the presence of −OH (bottom) in $MoS_2$ synthesis; (c) Calculated binding energy on sapphire (001) without (left) and with (right) the −OH groups. Reprinted with permission from Ref. [27]. Copyright 2019 American Chemical Society.

$MoS_2$ films to the substrate surface by modifying the surface chemistry and creating strong chemical bonds between the $MoS_2$ layer and the substrate. (iii) Surface activation: plasma treatment activates the substrate surface by creating reactive species, namely radicals, ions, and excited atoms or molecules. These species can enhance the surface energy and reactivity of substrate, facilitating the adsorption and decomposition of precursor molecules. Hence, plasma cleaning improves $MoS_2$ quality, including better uniformity, crystallinity and electrical/optical properties, by creating a clean and well-prepared substrate surface. Fig. 1a shows very different contact angles with and without this treatment. Adding a growth promoter to the molybdenum precursor solution before spin-coating in $MoS_2$ synthesis can enhance the growth process and improve the quality of the resulting $MoS_2$ films. Growth promoters are compounds or additives that facilitate nucleation and promote uniform growth [28, 29].

For example, alkali metal ions (*e.g.*, potassium, sodium) or surfactants can be added to the precursors solution to promote a uniform $MoS_2$ film formation. NaOH, specifically, can act as a complexing agent to stabilize the molybdenum precursor solution, enhancing its homogeneity and promoting uniform deposition during $MoS_2$ synthesis. NaOH can also modify the surface chemistry of the substrate, facilitating nucleation and growth of $MoS_2$ films [30]. The approach called $MoS_2$−OH bilayer-mediated method involves the preferential attachment of hydroxide groups −OH to the (001) surface of $MoS_2$, forming a $MoS_2$−OH bilayer structure during the growth (Fig. 1b) [27]. This technique promotes the growth of inch-sized monolayer $MoS_2$ on substrates like sapphire, mica, amorphous $SiO_2$, quartz (Fig. 1c) and various crystalline materials, including Si, SiC, $Si_3N_4$ and graphene, by inhibiting vertical growth along the [001] axis, thereby encouraging lateral expansion into larger areas. Additionally, the presence of hydroxide groups reduces sulfur vacancies and defects while protecting the $MoS_2$ surface from oxidation in air. This results in high-quality monolayer $MoS_2$ with a carrier mobility of up to ~ 30 $cm^2V^{-1}s^{-1}$. Hydroxides are not the only option designed for growth promoters, and other common choices are the halide salts. Ji Qingqing *et al.* [31] present experimental evidence indicating that the dynamics of $MoS_2$ growth are influenced by halogens, which is explained using the Brønsted–Evans–Polanyi relation. They propose a growth model that considers $MoS_2$ edge passivation by halogens, and this model theoretically replicates the observed experimental trends. In [22], the halogens present in the density gradient medium were shown to affect the lateral dimensions of the flakes.

### 2.2. Intentional doping of $MoS_2$

Liquid precursors allow a better control of the doping concentration than solid precursors. A dopant can be added to the molybdenum precursor solution to obtain specific functionalities or modify the properties of the synthesized $MoS_2$. These dopants can introduce additional electronic states, alter the band structure and thus influence the optical and electrical properties of $MoS_2$. Doping can also be carried out after $MoS_2$ synthesis by post-growth treatments, namely ion implantation [32] or plasma treatment [33]. The choice of doping method depends on the dopant species, the desired doping concentration and the synthesis conditions together with the compatibility with the overall CVD process.

Recently, the most common doping strategy is the addition of compounds to liquid molybdenum precursors. The kind of dopant depends on the desired modifications to the $MoS_2$ properties and the specific application requirements. 2D-$MoS_2$ has a heavily natural *n*-type conductivity attributed to the native sulfur vacancies [34]. The most common dopant for *p*-type doping is niobium available in the form of $NbCl_5$, soluble in nonpolar organic solvents, with a low melting point and a high solubility compared to $Nb_2O_5$ [35]. Another possibility to implement *p*-doping is the use of tantalum, even if until now the works reported in the literature concern only solid precursors, using $Ta_2O_5$ as in [36]. In contrast, for vanadium-based *p*-type doping, a diffuse water-soluble component is $NH_4VO_3$ [37]. Rhenium is mostly used to increase the conductivity by exploiting *n*-type behavior in reverse, especially as $NH_4ReO_4$ [38].

## 3. Photonic applications

As discussed above, the strong interest in 2D-$MoS_2$ application in photonics is due to its unique optical and electrical properties, namely a direct band gap, strong light-matter interaction and high quantum yield [39]. We will further review the main classes of light-based devices that have been proposed and developed in these last 10 years, also discussing their different ranges of applications.

### 3.1. Light-emitting devices

Due to the light emission of 2D-$MoS_2$ layers, the very first photonic device to be developed has been, quite obviously, the light-emitting diode (LED): almost ten years have passed since the fabrication of a vertical heterojunction composed of *n*-type monolayer $MoS_2$ and *p*-type silicon, which shows a low emission threshold power [40]. Following this achievement, other architectures for 2D-based LEDs have been reported, including metal-insulator-semiconductor junction, metal-semiconductor junction, and heterojunctions composed of various 2D materials. The advantages of this material for light-emitting devices concern its relatively strong photoluminescence and the possibility of controlling its action on the structural parameters, namely the number of layers and the scalability, as well as easy integration with other materials. However, one of the challenges for this type of device is related to insufficient emission performances, due to the low electroluminescence power of 2D materials, therefore, consistent research efforts are devoted to designing effective structures for increasing the external quantum efficiency, which is still limited to 12% [41]. Quite interestingly, $MoS_2$ monolayers have been used in other LED designs, exploiting the advantage of their high carrier mobility rather than their light emission. 2D-$MoS_2$ has been used for driving individual micro-LEDs by integrating thin film transistors based on this 2D material with other materials, which emit light, namely nitride micro-LEDs and organic LEDs [42]. The addition of $MoS_2$ to such device structure has been shown the significant improvement in the current density, brightness and carrier transport efficiency of the LED devices. Furthermore, the combination of $MoS_2$ with other materials, with the ability to generate the surface plasmons, allows for the modulation of its optical properties, enabling advanced applications, namely controlled light emission and ultrafast optoelectronic devices [43, 44]. These characteristics highlight the potential of $MoS_2$ for enhancing the performance and functionality of light emission devices, positioning it as a valuable material in the field of optoelectronics.

### 3.2. Photodetectors

Photodetectors based on 2D-$MoS_2$ have shown great potential in various applications, including sensing, communication, light-emitting diodes and optical modulators [45]. Their performance can be improved using metallic structures to take advantage of plasmonic effects [44, 46, 47] and by construction of heterojunctions [48]. Research has also focused on the development of large-scale 2D-$MoS_2$ photodetectors, demonstrating their feasibility for practical implementation. $MoS_2$-based photodetectors have been reviewed regarding their main performance metrics, namely responsivity, detectivity and response time, highlighting their potential for high-performance optoelectronic applications [49]. The first $MoS_2$ photo-transistor was demonstrated in 2015 [50], when, by using $MoS_2$ layers of different thicknesses, photodetection was tuned to different wavelengths with

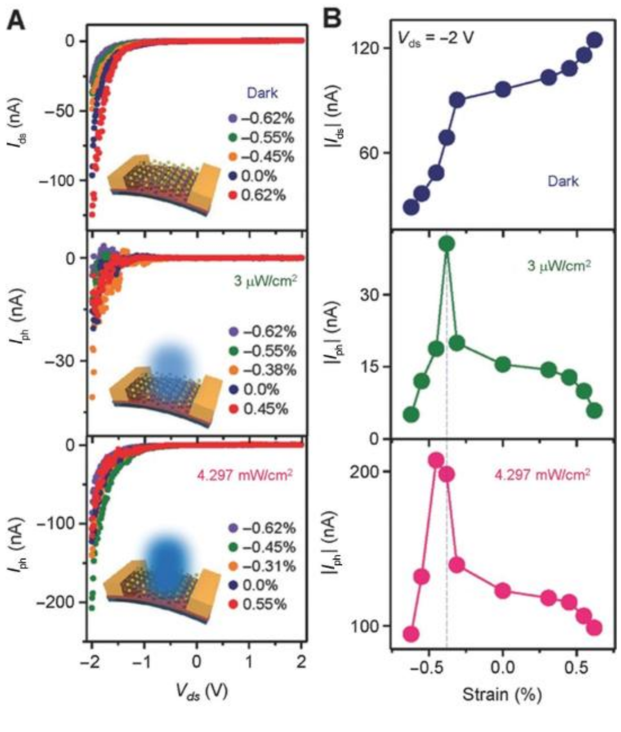


**Fig. 2.** (a) Electrical transport under different strains in the dark (top), with a low light intensity (middle) and a high light intensity (bottom). (b) Strain dependence of the dark current (top) and photocurrent (middle and bottom) under −2 V drain bias. Reprinted with permission from Ref. [51]. Copyright 2016 John Wiley & Sons.

very low dark current noise, one of the factors determining the detection limit of photodetectors. In 2016, a $MoS_2$ flexible photodetector based on single-layer material was reported, and the superior mechanical properties were coupled to a very efficient light detection [51].

Fig. 2 shows the strong strain dependence of the photocurrent, highlighting how it can be further modulated under different light intensities (Fig. 2a).

The authors discuss how these changes in transport and photodetection are caused by two following effects. The first one is the piezophototronic effect that manifests in the influence of strain-induced polarization charges on the transport of the charge carriers (Fig. 2b). The second one is the piezoresistive effect, where strain changes the band structure and the density of states of carriers, resulting in very different dependences of photocurrent on strain for different illumination conditions [51]. Furthermore, the integration of $MoS_2$ with other materials, namely oxide layers, has enabled the realization of high-performance monolayer $MoS_2$ photodetectors, displaying the potential for enhanced optoelectronic functionality. In particular, using a thin $Al_2O_3$ layer to induce tensile strain allowed for a strong improvement in both the photocurrent and responsivity [52]. The optical properties of $MoS_2$ photodetectors play a crucial role in determining their performance characteristics, namely band gap, which depends on the number of layers. The number of layers influences the optical absorption properties and, therefore, the efficiency of photodetection. The photonic properties of the 2D material, namely absorption characteristics, band gap modulation, and response to incident light, also affect the photoelectric performance of the photodetector in terms of detectivity, responsivity and response time. By leveraging and tailoring these optical properties, researchers can advance the development of high-performance $MoS_2$-based photodetectors for a wide range of optoelectronic applications.

### 3.3. Waveguides and optical cavities

2D-$MoS_2$ has gained attention due to its potential applications in elements for photonic circuits, namely waveguides and optical cavities. Its unique optical and electronic properties make it suitable for guiding and manipulating light at the nanoscale. Integrating 2D-$MoS_2$ with such photonic structures offers advantages, namely enhanced light-matter interactions, improved collection efficiency of emitted photons, and easy routing and manipulation of optical signals [53, 54]. In waveguides, a high refractive index of 2D-$MoS_2$ allows for strong light confinement and low loss, making it suitable for passive tunable coupling effects and loss tuning in resonators [55]. It can also be used to construct ultra-compact cavities with high-quality factors, enabling the control of spontaneous emission rates and the increase of exciton-photon coupling. Research has focused on engineering the photonic environment surrounding 2D materials, including 2D-$MoS_2$, to enhance their capabilities. This involves integrating 2D materials with nanocavities, metamaterials and metasurfaces to manipulate optical environments and improve light-matter interactions [39, 56]. The results obtained in this area of research have already allowed to design and develop flexible integrated photonic platforms where 2D-$MoS_2$ have been coupled to plasmonic nanocavities, planar photonic gratings and photonic waveguides [57, 58]. The integration of the $MoS_2$ layers on photonic structures has practical advantages for optoelectronic circuits, with large responsivity and tailored emission spectrum. This is critical for their use in optoelectronic and nanophotonic devices due to enhanced light-matter interactions, low-loss waveguiding and the construction of ultracompact cavities with high-quality factors. Therefore, strong research efforts are currently devoted to these hybrid systems, which is caused by a high potential for future advanced nanoscale optical devices and systems offered by the integration of 2D-$MoS_2$ with photonic structures.

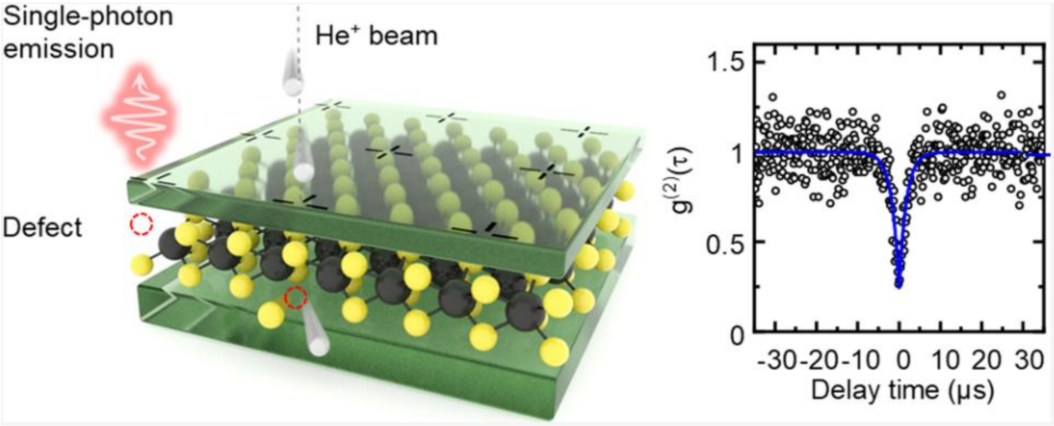


**Fig. 3.** Schematic illustration of the $MoS_2$ structure where single photon emission is obtained by generating defects using the focused ion beam (left) and the second-order correlation $g^{(2)}(\tau)$ function demonstrating emission of single photons (right). Reprinted with permission from Ref. [63]. Copyright 2021 American Chemical Society.

### 3.4. Single photon sources

The efficient light emission of single layers of $MoS_2$ is also attractive for developing one of the fundamental devices of quantum photonics technologies: the single-photon emitter that provides on-demand, deterministic photonic qubits. Various methods are available for obtaining light quanta, but solid-state devices are of particular interest due to their scalability and easy integration into current photonic platforms. Nanostructures, namely quantum dots, isolated defects in semiconductors, and color centers in diamonds are some of the most successful systems proposed so far [59, 60], with many 2D materials currently being explored for these applications, considering the emission of single photons by isolated defects in hBN, $WSe_2$ and other van der Waals materials [61, 62]. Concerning $MoS_2$, recent research has made significant progress in the development of single-photon sources based on atomically thin $MoS_2$. The generation and control of single photons has been demonstrated by considering isolated defects in this material that can be deterministically realized by external irradiation by a focused ion beam (Fig. 3) [63].

Another interesting option for the realization of isolated quantum emitters is related to the ascertainment of quantum confinement of electrons in the 2D semiconductor layer. This confinement has been claimed to be realized by strain gradients applied to the 2D monolayer [64], however, very recently it has been demonstrated that single photon emission from such strained 2D layers might be related to the generation of defect states [65]. On the other hand, it has been argued that quantum confinement can be realized in 2D nanostructures of very small sizes, leading to the effective realization of $MoS_2$ quantum dots (QDs), although the emission of single photons from such structures is yet to be reported [66, 67].

These results highlight many interesting advantages of 2D materials for the development of single-photon sources, namely the possibility of room-temperature operation, high-photon count due to the high brightness, electrically triggered generation, low excited-state lifetime, polarized emission, and optically addressable electron spin state. The mentioned features, already demonstrated by single photon emitters in 2D materials, indicate that these devices should have great potential for many applications in quantum photonics.

## 4. Conclusions

This work provides a comprehensive overview of the current research on 2D-$MoS_2$ for photonics. We have highlighted the peculiar properties of 2D-$MoS_2$, namely direct band gap and tunable optical properties that motivate the development of photonic devices based on this material. Additionally, we have presented the most recent results in preparing this material by CVD, focusing on the most impactful breakthrough achieved in these last years, including the introduction of metallic liquid precursors and the options to tackle another relevant issue, the control of doping. Furthermore, we have provided a complete scenario of the development of various types of light-based devices with account of the advantage of the peculiar properties of $MoS_2$ to improve the performances for various applications. It is foreseeable that this material will continue to attract strong research interest and that the mass production of 2D-$MoS_2$ photonic devices might be established quite soon. Despite significant advancements in the field, challenges remain, including material quality, reliable doping, device scalability, and integration issues. Overall, it can be argued that its potential in photonics is extensive, foreseeably driving advancements within a wide range of technological applications.

**Funding and Acknowledgements**

The authors acknowledge the funding by the Italian Minister of Research (MUR) within the PRIN2022 project “2DIntegratE” (2022RHRZN2). Dr. S. Golovynskyi acknowledges the Key Research and Development Project of Guangdong Province (2020B010169003) for partial support.

**Declaration of competing interest**

The authors declare no competing financial interests or personal relationships to the reported paper.

**Data availability**

The reported data can be available on request to the corresponding authors.

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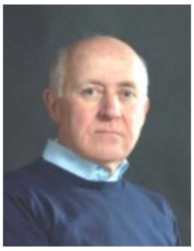

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**Двовимірний $MoS_2$ для застосувань у фотоніці**

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**Анотація.** Двовимірний дисульфід молібдену ($MoS_2$) викликав значний інтерес у галузі оптоелектроніки завдяки своїй прямій забороненій зоні, регульованим оптичним властивостям і потенціалу для реалізації гетероструктур Ван-дер-Ваальса. У цій статті ми пропонуємо комплексний огляд 2D $MoS_2$ і його застосування у фотоніці. Ми починаємо з обговорення прогресу в синтезі $MoS_2$ способом «знизу-вверх» за допомогою хімічного осадження з парової фази, фокусуючись на нових підходах з використанням рідких прекурсорів молібдену. Потім ми розглядаємо останні розробки у світлових пристроях на основі $MoS_2$, включаючи світловипромінювальні діоди, фотодетектори, хвилеводи, оптичні резонатори та однофотонні джерела випромінювання. Підсумовуючи останні досягнення, цей огляд дає уявлення про перспективи застосування $MoS_2$ у фотоніці.

**Ключові слова:** фотоніка, 2D матеріали, дисульфід молібдену, хімічне осадження з газової фази, рідкий прекурсор.