Chapter 1

Medical Geology Molybdenite as a TMDC 2D-Nanomaterial in Healthcare Applications

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This literature review explores molybdenite (MoS_2), a representative transition metal dichalcogenide (TMDC) in nanotechnology involving two-dimensional (2D) materials, and its potential applications in healthcare devices. The chapter begins by discussing the concepts of mineral nanotechnology and the unique properties of TMDCs. It then examines the role of molybdenum in biological systems, highlighting its low toxicity. Following this, a range of general and biomedical applications of both synthetic and natural MoS_2 are presented, encouraging a discussion on how 2D molybdenite can potentially be applied in health-related devices. The review concludes that mineral precursors have a limited use in biomedical nanotechnology due to impurities and structural defects, which often cannot be fully resolved. However, these imperfections may also facilitate functionalization, a common approach for processing MoS_2 in healthcare applications. Finally, it is emphasized that there is a significant lack of interdisciplinary studies integrating mineralogy, petrology, geochemistry, and medical geology with a nanotechnological perspective for biomedical purposes. Promoting this research area could advance the development of new healthcare devices.

Keywords: Mineral nanotechnology, Applied mineralogy, Medical mineralogy, Biomedical mineralogy, Van der Waals minerals.

1.1 Introduction

Molybdenum was discovered in 1778 by the Swedish chemist Carl Wilhelm Scheele and first isolated by Peter Jacob Hjelm in 1781. Its name originates from molybdenite, the most abundant molybdenum-bearing mineral, which was first classified by Johan Gottschalk

Wallerius in 1747. The term “molybdenite” derives from the Greek word "molybdos" which means "lead-like", due to the historical confusion of the mineral with lead ores [1, 2].

Molybdenite (molybdenum disulfide - MoS_2) is a mineral in the hexagonal crystalline system, characterized by its prominent basal cleavage. It consists of molybdenum atoms bonded covalently to sulfur atoms with bond length of 2.41 Å, forming layers that are 0.65 nm thick. These layers are held together by weak Van der Waals forces [3] and [4].

The isolation of thin layers composed of strongly bonded atoms, typically less than 100 nm thick, by breaking weak Van der Waals interactions in crystalline structures forms the foundation for two-dimensional (2D) nanomaterials, which are often produced through top-down processes [5] and [6]. This field gained significant attention in 2004 with the isolation of graphene from graphite and the discovery of its remarkable properties, including electrical superconductivity at room temperature [7].

Several minerals with Van der Waals interactions, such as graphite and phyllosilicates, have become important sources for 2D nanomaterials [8]. Among these, transition metal dichalcogenides (TMDCs) are particularly notable, as they can be easily cleaved to form layers less than 100 nm thick [9] and [10]. TMDCs have the general formula MX_2, where M represents a transition metal from groups IV (e.g., Ti, Zr), V (e.g., V, Nb, Ta), or VI (e.g., Mo, W), and X is a chalcogen (S, Se, or Te). These elements are arranged in an X-M-X structure, with each metal atom bonded to two chalcogen atoms in hexagonal packing [9], [11] and [12].

This review explores the role of molybdenite in medical geology and mineral nanotechnology, with a focus on its potential applications as a 2D material in healthcare. It provides an overview of fundamental concepts in 2D mineral nanotechnology, the biological functions of molybdenum, its low toxicity, and various potential applications of both synthetic and natural MoS_2 in nanotechnology.

1.2 TMDCs and 2D-mineral nanotechnology

Mineral nanotechnology focuses on developing devices and processes using natural solid nanomaterials (rocks, minerals, and non-minerals) that undergo little to no beneficiation [13]. Specifically, the field of 2D mineral nanotechnology investigates minerals with placoid structures and high surface area-to-thickness ratios, where the thickness can be reduced to less than 100 nm from bulk geological material [14].

2D-nanotechnology originated with the micromechanical exfoliation of highly oriented pyrolytic graphite (HOPG), a synthetic material known for its high crystalline purity, from which graphene was first isolated and characterized [15]. Since geosciences focus on the study of natural minerals, the implications of graphene isolation led to two main areas in mineralogy: (i) the production of nanostructured devices directly from mineral resources [16] and [17]; and (ii) the extraction of 2D-minerals directly from geological deposits [18] and [19].

The branch of mineral nanotechnology is exclusively concerned with processes for Mineral nanotechnology primarily involves top-down processes to obtain nanomaterials from bulk mineral precursors, as the geological conditions under which crystal growth occurs typically result in multilayer structures [20] and [21]. However, certain metamorphic and tectonic conditions can stabilize minerals in a 2D form within geological environments [13] and [14].

The study of 2D nanomaterials began with native elements, with the exfoliation of graphite to obtain graphene (carbon-based materials). While other native elements, such as antimony [22], bismuth [23], selenium [24] and tellurium [25], have similar structures, they are not the only candidates for 2D materials [8]. Among silicates, the largest class of minerals in the Earth's crust, phyllosilicates — such as clay minerals [26] and [27], micas [28] and chlorites [29] — are notable, as their planar layers are held together by Van der Waals forces. Other minerals classes, including sulfosalts [30], oxides [31] and [32], phosphates [33] and carbonates [34], also have a crystalline structure suitable for 2D materials obtention [8] and [35].

Molybdenite, the TMDC analyzed in this work, belongs to the sulfides mineral class. Another TMDC sulfide with recent prominence in 2D nanomaterials research is tungstenite (WS_2) [36] and [37]. In addition, non-TMDC sulfides such as orpiment (monoclinic As_2S_3) [38], anorpiment (triclinic As_2S_3) [39], stibnite (Sb_2S_3) [40], and getchellite ($AsSbS_3$) [41] have also gained attention.

The properties of TMDCs have been studied since the 1960s [42]. These materials are known for their photoelectrochemical [43], thermoelectric [44] and tribological [45] properties, but gained renewed interest as 2D materials due to their differences from graphene [46]. One major distinction is the absence of a bandgap in graphene's electronic structure, which led researchers to search for 2D semiconducting materials. In this context, TMDCs gained interest because they can be scaled down to the nanometer level, including 2D structures, with a direct bandgap, strong spin-orbit coupling, and favorable electronic and mechanical properties. Due to its robustness and natural abundance, molybdenite has become the primary TMDC of interest for 2D mineral nanotechnology.

Although natural minerals often contain crystalline defects and impurities, mineral nanotechnology emphasizes the potential of these materials with minimal beneficiation. This approach avoids costly synthesis processes and aims to make nanomaterials available in abundant, affordable forms [13]. These principles highlight the potential of molybdenite as a raw material for biomedical devices, a topic that will be explored further in this article.

1.3 Considerations of molybdenum in living systems and medical geology

Molybdenum is an essential trace element for several living organisms, including humans, and is the only metal in the 4d row (second transition series) of the periodic table with known biological activity [1]. Its biological significance was first identified in enzymes such as nitrogenase, nitrate reductase, and xanthine oxidase, highlighting its role as a crucial catalyst in their active sites [48].

Nitrogenase is the enzyme responsible for the reduction of atmospheric nitrogen (N_2) to ammonia (NH_3), a key process in nitrogen-fixing bacteria found in soil [49]. Nitrate reductases facilitate the reduction of nitrate to nitrite, playing a vital role in the nitrogen assimilation of plants [50]. Xanthine oxidase is involved in the catabolism of purine bases, converting them into uric acid, a process that occurs in humans as well [51]. To date, over 50 different molybdenum-dependent enzymes have been identified [48].

Molybdenum is not found in its metallic form in nature and is typically consumed in molecular form, predominantly as Mo (IV) or Mo (VI) species. Cases of molybdenum poisoning (molybdenosis) in humans are rare, primarily due to its relatively low toxicity. Acute symptoms require the ingestion of doses 1,000 times higher than the recommended daily intake over an extended period. The kidneys efficiently filter and eliminate molybdenum from the body, with the process usually completed within a few weeks [52].

Although symptoms such as gout and pneumoconiosis have been linked to high molybdenum exposure, the studies conducted have not conclusively established a dose–effect relationship. However, copper deficiency has been shown to increase susceptibility to molybdenum toxicity in humans, similar to what has been observed in ruminants like cows and sheep, where excess molybdenum leads to symptoms resembling copper deficiency [52] and [53].

Nutritional molybdenum deficiency is also rare in humans and is typically associated with patients undergoing prolonged parenteral feeding, newborns, or individuals with conditions that cause severe molybdenum malabsorption or excessive excretion. The daily requirement for molybdenum in a traditional human diet is only 45 μg, and it is readily available in grains, vegetables, and meats. Most diets can easily provide safe and adequate levels of this element [54].

Due to its low toxicity (as it is efficiently eliminated from the human body) and its role as an essential micronutrient, molybdenum is well-suited for use in healthcare devices. As molybdenite, its most common mineral form, can function as a 2D material, there is potential to explore nanotechnological applications of low-dimensional molybdenite in biomedical contexts.

1.4 General applications of synthetic and mineral 2D-MoS_2

Monolayer molybdenite, or even a few layers (broadly defined as 2D material), has emerged as a promising nanomaterial for a wide range of applications. It is highly suitable for use in sensors, exhibits photocatalytic properties that can be utilized for environmental remediation and self-cleaning materials, and plays a role in hydrogen energy generation and storage. Additionally, it can be used as an additive in 3D printer ink, functionalized for various purposes, and applied in electrical and electronic devices due to its semiconductor properties [55] and [56].

One notable property of 2D molybdenite is its ability to absorb electromagnetic radiation from the visible spectrum, making it ideal for photosensor applications. A major challenge in developing high-performance broadband photodetectors is the requirement for materials with narrow spectral sensitivity. Even molybdenite sourced from mineral origins performs well in heterostructured systems for this purpose [57]. For instance, when combined in thin films with WSe_2 (another TMDC material) or epitaxially grown on gallium nitride (GaN), MoS2/WSe2 heterostructures produce highly sensitive photodetectors that cover the visible-near infrared (NIR) spectrum, while GaN combined with monolayer molybdenite can cover the ultraviolet (UV) to NIR spectrum [57], [58] and [59].

Environmental applications of 2D molybdenite fall into four major categories: (I) adsorption of contaminants, (II) environmental sensors, (III) photocatalytic degradation of pollutants, and (IV) separation or filtration membranes [60]. In group I, 2D molybdenite has been used for the adsorption of heavy metal ions (e.g., Hg^{2+}) [61] and organic contaminants such as dyes and oil [62] and [63]. For group II, synthetic MoS2 has been employed as a sensor for detecting formaldehyde gas in indoor environments [64]. An example of group III is the production of a synthetic MoS2 pyramid using chemical vapor deposition (CVD), which demonstrated a lower bandgap and greater bactericidal activity than most TiO_2-based photocatalysts for water disinfection [65]. Group IV includes composite materials made from 2D molybdenite obtained via top-down processes from mineral precursors, which exhibit strong hydrophobic properties, good weather resistance, and potential for use in self-cleaning devices [66] and [67].

Hydrogen production via water-splitting reaction shows great potential for green energy generation as a replacement for fossil fuels. This process requires a high enthalpy (237 kJ/mol), so reducing energy consumption is critical for making it economical. 2D molybdenite has been proposed as a catalyst for this reaction, due to its thermoneutral hydrogen-binding energy and highly active H_2 evolution sites [68]. Additionally, it can adsorb and diffuse hydrogen within its structure [69].

In polymer dispersions, molybdenite nanoparticles have been used as crosslinking agents, facilitating polymer bonding via click chemistry in 3D-printer inks based on poly N-isopropylacrylamide-co-acrylamide-co-2-mercaptoethylacrylamide (PNAM) [70] and [71].

Functionalization of molybdenite nanosheets modifies their original properties to tailor them for specific uses. For example, doping 2D molybdenite with CdS nanoparticles enhances its photoactivity for optoelectronic applications [72], while functionalizing it with niobium nanoparticles progressively shifts its electrical properties from semiconductor to conductor [73].

Monolayer molybdenite's direct bandgap structure enables lower energy consumption than traditional transistors, making it suitable for use in supercapacitors [74] and [75]. Additionally, piezoelectricity in 2D materials, which had been negligible for technological applications, became significant following the discovery of piezoelectric properties at monolayer molybdenite grain boundaries. This breakthrough enables the production of flexible and thin piezoelectric devices [76].

From this broad range of applications, the next section will focus on specific adaptations of these properties for healthcare devices, exploring the potential of using mineral-origin MoS_2 as a raw material.

1.5 Healthcare considerations and potentials applications of 2D molybdenite

2D-MoS_2 can be employed in healthcare devices for both therapeutic and diagnostic purposes, which can be categorized into seven key areas: (I) drug delivery, (II) gene delivery, (III) phototherapy, (IV) combined therapy, (V) bioimaging, (VI) theranostics, and (VII) biosensors, as outlined below [77].

Drug delivery refers to processes that enhance the precision and targeting of drug administration within the body. Several uses of 2D-MoS_2 derived from minerals have been explored in this area [77]. To ensure patient safety, molybdenite must be thoroughly characterized to eliminate impurities. In one instance, molybdenite nanosheets were functionalized using copolymers via surface modification (mussel-inspired chemistry) and single-electron transfer living radical polymerization. This nanocomposite demonstrated the ability to load and selectively deliver cisplatin, an anticancer agent [78]. Additionally, theoretical studies have shown that MoS2 nanosheets can adsorb and selectively release antituberculosis drugs with robust stability, releasing the drug at high temperatures and in acidic environments [79].

Gene therapy involves the delivery of specific genes to the cell nucleus, with the goal of treating certain cancers and other genetic disorders. Synthetic monolayer MoS_2 has been investigated as a gene delivery agent. Functionalized monolayer MoS_2 has demonstrated efficiency in co-delivering RNA to pancreatic cancer cells, with low toxicity and high efficacy in gene delivery [80].

There are two primary phototherapy techniques that utilize MoS_2 nanotechnology: (i) photodynamic therapy (PDT), in which photosensitizers are activated by light at specific wavelengths to generate reactive oxygen species that induce cell damage and apoptosis, and

(ii) photothermal therapy (PTT), where biomedical agents convert near-infrared (NIR) radiation into heat to ablate targeted cells [81].

Combined therapy involves the use of multiple treatment modalities (e.g., chemotherapy, phototherapy, radiation therapy, and immunotherapy) to enhance therapeutic outcomes. MoS_2's properties—such as its photo- and thermo-activity, functionalization potential, and drug delivery capabilities—make it a promising candidate for such therapies. However, the current research is primarily in preliminary stages, focusing on synthetic MoS_2 for cancer treatment [82].

Bioimaging devices are used for diagnosing cellular and tissue properties and monitoring the real-time distribution of intracellular nanoparticles and drugs. Single-layer MoS_2 efficiently emits photoluminescence under visible light excitation. When combined with substances such as chitosan, it shows great potential for real-time, deep, multiphoton, and three-dimensional bioimaging using low-power laser excitation [83].

Theranostics, a growing field in healthcare, combines therapy and diagnostics synergistically — especially through the use of nanomaterials. It has proven relevant in identifying and treating tumors, including metastatic cases, and in addressing other conditions like osteoarthritis [84]. MoS_2 nanosheets conjugated with hyaluronate (HA) have shown potential for theranostic applications, where HA facilitates MoS_2 delivery to cancer cells via endocytosis. Once inside the cell, MoS_2-HA and MoS_2, when excited by NIR radiation, induces cell ablation. This composite can also be easily detected using photoacoustic or photoluminescence imaging, enabling diagnosis and accumulation in cancer cells at levels higher than those observed in the liver or kidneys [85].

2D molybdenite possesses properties that make it highly suitable for biosensors, such as its ability to accommodate various chemicals and biospecies. Molybdenite-based biosensors can be classified into four categories [86]:

- (I) Electrode-based biosensors detect changes in charge or mass on the molybdenite surface, generating signals due to changes in transconductance. These sensors can detect proteins, DNA, and other biochemical compounds [87].
- (II) electrodeless-optical biosensorsanalyze photoluminescence loss or changes in surface roughness and permittivity caused by biomaterials [88].
- (III) reverse-electroluminescent biosensors detect changes in photoluminescence resulting from the adhesion of key biological ions (H^+, Li^+, Na^+ and K^+) , enabling the measurement of ion concentrations [89].
- (IV) other biosensors involve composites with materials like graphene, carbon nanotubes, metal nanoparticles, and various polymers for specific applications [90].

Further uses of 2D-MoS2 include the production of antibiotics to combat resistant bacteria [91] and [92], external sensors for monitoring health parameters [93], and the development of disinfectant nanocomposites [94].

1.6 Conclusions

Molybdenum is an essential trace element for various living organisms, including humans, and is known for its low toxicity. Its most abundant mineral form is molybdenite (MoS_2) a transition metal dichalcogenide (TMDC). Molybdenite exhibits several valuable properties, including a large surface area, tunneling energy bands, reasonable electronic mobility, photoluminescence, stability in liquids, low toxicity, and a layered crystal structure. Its potential as a 2D material arises from these flat layers, which are held together by van der Waals forces and can be separated through top-down processing methods.

This review highlights a growing number of attempts to use molybdenite as a raw material for MoS_2-based nanotechnological devices, particularly for robust applications such as environmental remediation, where large quantities of 2D material are required or where highly sensitive electronic behavior is not essential, as in biosensors.

While synthetic 2D-MoS_2 production methods are more costly than extracting the material through systematic cleavage of molybdenite, refining natural molybdenite to achieve the high crystallographic quality and purity required for certain applications is often even more expensive and sometimes impossible, as it is difficult to eliminate all the structural defects in the natural mineral. This challenge leads many researchers in nanotechnology to prefer synthetic precursors.

Using synthetic materials in laboratory testing allows for a more comprehensive exploration of a material's potential. However, it represents only a small step toward making these devices widely available to the public. In healthcare, where patient safety is paramount, devices must be carefully designed to avoid any risk of unintended or harmful behavior that could worsen a patient's condition. On the other hand, defects and impurities in natural molybdenite can aid its functionalization, thereby enhancing its potential for nanotechnological and biomedical applications.

A thorough geochemical characterization of the natural environments where molybdenite is found may be key to better understanding its potential applications. Few studies exist at the intersection of mineralogical-petrological characterization and nanotechnology applications, but such efforts could help popularize the use of these devices.

It is essential for mineralogists and petrologists to align their work with the specific raw material demands of healthcare specialists. Collaboration between multidisciplinary teams will be critical for advancing the research and development of 2D-molybdenite-based devices, as well as other 2D minerals, and making them more widely available.

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