IOSR Journal Of Applied Physics (IOSR-JAP)
e-ISSN: 2278-4861.Volume 14, Issue 5 Ser. I (Sep. – Oct. 2022), PP 01-06
www.Iosrjournals.Org

Two-dimensional transition metal dichalcogenides nano materials and their Applications.

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Abstract
This article reviews on Two-dimensional transition metal dichalcogenides nanomaterials and their Applications. Recent advances in two dimensional metal dichalcogenides have subjected its attention to a variety of fields such as optoelectronics, nanoelectronics, sensors, energy storage etc.These materials are finding numerous applications for next generation electronics and electronic devices.There are many methods for sample preparation such as the mechanical,liquid exfoliation and CVD techniques.In this review,the properties,preparation methods and applications of TMDnanomaterials are discussed.

Key Words
Two dimensional transition metal dichalcogenides, Mechanical properties, Electronic and optical properties, synthesis techniques, Energy storage, Electronic devices, Supercapacitors.

Date of Submission: 20-08-2022 Date of Acceptance: 04-09-2022

I. Introduction

In recent years 2- Dimensional nanomaterial Graphene,hexagonal boron nitride has gained importance which led to exploration of other 2D nanomaterials[1-5].Graphene exhibits semi-metallic properties. The semi-conducting and insulating 2D nanomaterials having structural properties which are used to integrated in nano electronic devices for various applications.Recently 2-D transition metal dichalcogenides having a structural formula MX_2 where M is a transition metal element (Mo,W, V, Nb, Ta, Ti, Zr, Hf, Tc, and Re)and X is a chalcogen element (S, Se, Te) as shown in Fig.1.The MX_2 consists of three atomic layers X-M-X in which central layer was sandwiched between 2 chalcogen atom layers.The stacking of these layers resemble graphite structure [6].These layers are bonded with vanderwaal's force that contributes the formation of monolayers or nanolayers via exfoliation.The 2DTMD's nanomaterials possess large surface area to volume ratio,different phases, defects and edge enrichment strategies.Also direct band gap ,strong spin -orbit coupling,are due to quantum confinement.This behaviour gained them to exhibit excellent electronic and optical properties which further featured them to be used in electronic devices, optoelectronic devices, gas sensing devices, energy storage devices etc[7-15].In this review, we discuss the properties,preparation methods and various applications of 2D TMD's materials.

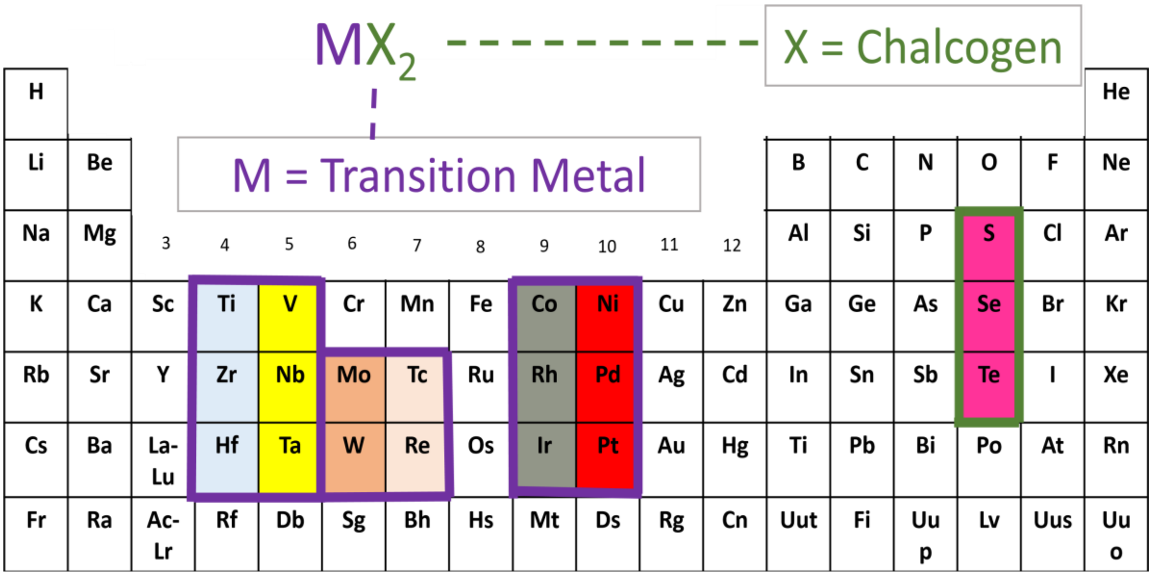

Fig 1 Periodic table indication 16 transition metals and 3 chalcogen atoms.

II. Properties

2.1 Fundamental Crystal structure

The 2 D TMD's nanomaterials have a layered structure by following the stoichiometry MX_2 where M is a transition metal and X is a chalcogen.The transition metal atoms and chalcogen atoms are in a plane having covalent bond between them. Among the layers ,there is a vanderwaals bond which is weak in nature. The 2D TMD's has gained importance due to the contribution of d sub shell electrons in d orbital.The oxidation states of transition metals and chalcogens are +4 and -2 respectively.Thus the number of d sub shell electrons varies between 0 and 6 as we move from group IV to group X.Depending on the arrangement of structural atoms (X-M-X),single layer of TMD's can possess a different phase structures.They can be considered as three atomic layers located on top of each other and perpendicular to layer.The distribution of electrons in d sub shell of transition metal atom plays a key role in deciding phase structure of TMD's[16].The completely filled d-sub shell orbitals decides the semi-conductor behaviour and partially filled d-sub shell gives rise to metallic nature of 2 D TMD's nanomaterials.It has been reported that according to the structure of unit cell, single layer of TMD's can be trigonal prismatic also known as 2H phase and octahedral phase i.e 1T phase depending on the occupancy of electrons in d sub shell.

2.2 Mechanical Properties

The TMD's are mechanically flexible and stronger similar to Graphene.The elastic properties of MoS2 nano sheets are reported.It has been observed that the young's modulus of MoS_2 nanosheets are exceptionally high.Another [17] the stiffness and breaking strength .The strength of strongest single layer membrane is 11% of their young's modulus. This indicates that the material is defect free and crystalline in nature. The study of mechanical properties of TMD's helps in understanding the appropriate nature so that the materials can be used as reinforcing materials in composites. This helps in fabrication of flexible electronic devices[18].

2.3 Electronic and Optical properties

The electronic properties are controlled by filling of non bonding d bands for the groups IV to groupX. The impact of chalcogen atom is small when compared to metal atoms. But as the atomic number of chalcogens is increased, the broadening of d band increases which results in the decrease of band gap.[11,12] reported that the bulk TMD's possess indirect band gap. But as the semi-conducting materials are tuned by phase engineering ,the indirect band gap materials turns into a direct band gap monolayer material[13-18].This kind of feature improves catalytic performance.Also the optical absorption characteristic is related to band structure of semi-conducting layered materials.The electronic character of different layered materials are given in table 1 below.To tune the band gap the materials are often doped/alloyed or mechanically strained or stacked in the form of hetero structures with other elements. Out of many ,doping/alloying is a scalable route to modify the band gap.

Table 1 Electronic character of different layered TMDs [16]

Group	M	X	Properties
4	Ti, Hf, Zr	S, S, Te	Semiconducting (Eg = 0.2 ~ 2 eV)
5	V, Nb, Ta	S, Se Te	Narrow band metals or semimetals
6	Mo, W	S, Se Te	Sulfides and Selenides are semiconducting. Telurides are semietallic.
7	Tc, Re	S, Se Te	Small gap semiconductors.
10	Pd, Pt	S, Se Te	Sulfides and Selenides are semiconducting. Telurides are metallic. PdTe2 is superconducting

III. Synthesis of 2D TMD's

Single or few layered 2D TMD's can be synthesized by several methods.These methods can be divided into Top-down and Bottom-up approaches.

3.1 Top-Down approach

3.1.1 Mechanical Exfoliation

This was used to exfoliate graphene layers[19].this method gives good quality of atomically thin 2D TMD's. It was reported that the crystallinity will be maintained after the exfoliation from bulk structures[20-22].

3.1.2 Liquid Exfoliation

Bulk crystals are exfoliated vis ultrasonicationin specific solvent.The weak vanderwaal's forces are broken down by sonication but not strong covalent bonds[23].The solvent molecules help to stabilize exfoliated nanosheets and inhibit their reassemble.These molecules try to bind the surface of nanosheets with their existing surface energy via vanderwaal's interaction .Multiple layers of 2D TMD's are synthesized such as MoS_2,Ws_2,$TaSe_2$ etc are reported[24-26].

3.1.3 Chemical Exfoliation

In this method the intercalators are introduced into the layers of bulk crystals through ultrasonication. Then the bulk TMD's are exfoliated into ultrathin nanosheets under sonication. Without using toxic organic solvents 2D TMD's can be synthesized.

3.2 Bottom -up approach

3.2.1 Chemical vapour deposition

In this technique,the reaction precursor are exposed tosubstrate under high temperature and pressure.The reaction between transition metal atoms and chalcogeneide atoms generate ultra thin 2D TMD's.The obtained reaction product was deposited on substrate[27].The use of substrate increases the transfer process of nanosheets.This synthesis method provides quality and excellent electronic property.

3.2.2. Pulsed Vapour deposition

In this method , a laser beam is used to ablate the particles of desired material from their bulk structureand then ablated particles are condensed on the desired substrate.Faster growth rate can be achieved due to laser beam. The temperatue and time for growth rate is less when compared to CVD technique.

Serna *et .al* studied theeffect of cutting down the temperature from 700 ˚C to 300 ˚C and they obtained that the stoichiometric ratio ofMo to S elements is affected at relatively lower temperatures with lack of S atoms.[28] Tian *et al* grew 1-cm-scale2D monolayer WS2 on sapphire at a temperature of 500 ˚C which is lower than the temperature used for the growthof MoS_2(700 ˚C). They observed that the quality of the 2D monolayer WS_2 thin film was improved after annealingit in sulphur rich environment.[29]

3.2.3 Solvothermal method

With the help of precursors under the condition of specific solvent and specific reaction time,ultrathin 2D TMD's can be obtained[30].It was reported that the ultrathin MoS_2 and WS_2 nanosheets are obtained after the reaction of Molybdic acid or tungstic acid with thiourea at 773 K for 3h.High yield can be achieved with low cost.This technique is promising for industrial applications of 2D TMD's[31,32].

IV. Applications of 2D TMD's

4.1 Electronic devices

Single layer MoS_2 nanosheets are seem to be supplementary material to graphene when used in low power electronic devices.MoS_2[2,33] shows excellent semi-conducting properties due to its direct band gap of 1.83 eV.The carrier mobility,current of MoS_2 based devices can be increased to 200 cm^2V^{-1} S^{-1}.Also Multilayer MoS_2 shows more advantages when compared to single layer MoS2.Thus 2D TMD's can be used as potential building blocks for various integrated circuits and various electronic devices[34,35,36].

4.2 Energy storage applications

The energy storage devices and their techniques play vital role for the sustainable development of technologies. As 2D TMDs has atomic thin layered structure, high surface to volume ratio and electrochemical properties has made them suitable for energy storage applications such as lithium-ion batteries, super capacitors, etc. This behaviour of 2D TMD materials[37-39] towards energy storage is due to their layered structure makes it suitable as more active sites are present .

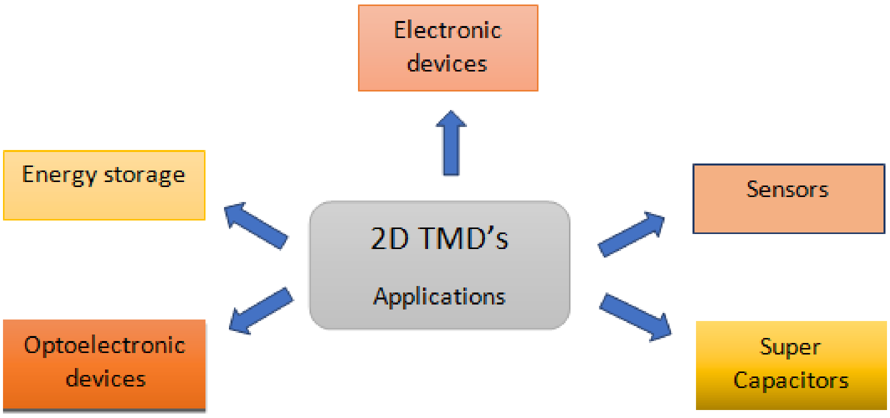

Fig 2. Various applications of 2D TMD's

Also high surface area to volume ratio makes them appropriate for energy storage by combining with surface properties and conductivity.

4.3 Super capacitors

Supercapacitors known as electrochemical capacitors are currently under development. When external voltage is applied to the similar electrodes, some ions get adsorbed in case of few electrodes. This results in pseudo capacitance.Usually the pseudocapacitors are prepared by using transition metals.The stacked like structure of TMDs for example MoS_2 has large electric double layer capacitance and large pseudo capacitance because of different oxidation state of the metal atom which makes it as a promising for energy storage device. Super capacitors are the promising energy storage devices for high power applications such as electronic devices, hybrid electric vehicles, regulating power supply for battery separation .Due to small flake size, uncontrollable thickness and various defects it has limited production[40-43].

4.4 Sensor applications

2D TMDs are considered to have efficient sensor application due to its unique Properties. The atomic level thickness and high surface to volume ratio makes them potentialto analyze and detect a large amount of foreign particles. Also TMDs are highly active and show rapid response towards the target particles. Able to recover with the application of low energy or power[44,45].It has been reported that the 2D single monolayer MoS_2 has a great application as chemical sensor which exhibits photo response as well as ultralow standby power dissipation at room temperature.

Apart from chemical sensor,MoS_2 nanoparticle modified electrodes may act like a glucose sensor. In the field of biomedical and disease diagnosis, detection of specific DNA or peptides sequences have great importance, and to perform the detection, it requires an ultrasensitive DNA sensor. Single layer 2D MoS_2 has the sensitivity towards the biomolecules with fluorescence probe. Hetero-structure of graphene/MoS_2 has an ultra-sensitivity towards the detection of DNA hybridization.[46,47] Most of the 2D TMDs sensors are realized with the use of mechanically exfoliated or liquid phase exfoliated MoS_2 flakes.

V. Conclusion

In summary, we discussed the various properties structural,mechanical and electronic of 2D TMD's. 2D TMD's can be synthesized by various methods like Mechanical exfoliation, Chemical exfoliation, liquid exfoliation, CVD,PVD, Solvothermal methods.Numerous applications are there for these materials in all the fields due to their atomic thickness and high surface to volume ratio. Few major areas of 2D TMD's are discussed such as electronic devices,energy storage, supercapacitors, sensor applications.

Acknowledgements

The authors acknowledge to CDC committee and Management of VNR Vignana Jyothi Institute of Engineering and technology.

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Rajani .T, et. al. "Two-dimensional transition metal dichalcogenides nano materials and their Applications." *IOSR Journal of Applied Physics (IOSR-JAP)*, 14(5), 2022, pp. 01-06.