**Graphene to Advanced MoS$_2$: A Review of Structure, Synthesis, and Optoelectronic Device Application**

Tahreem Nawz $^1$, Amna Safdar $^{1,*}$, Muzammil Hussain $^2$, Dae Sung Lee $^{2,*}$ and Muhammad Siyar $^1$

1 Department of Materials Engineering, School of Chemical and Materials Engineering, National University of Sciences and Technology, H-12 Islamabad 44000, Pakistan; tnawz.nse6@scme.nust.edu.pk (T.N.); muhammad.siyar@scme.nust.edu.pk (M.S.)

2 Department of Environmental Engineering, Kyungpook National University, Daegu 41566, Korea; muzammil@knu.ac.kr (M.H.); daesung@knu.ac.kr (D.S.L.)

* Correspondence: amna.safdar@scme.nust.edu.pk

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**Abstract:** In contrast to zero-dimensional (0D), one-dimensional (1D), and even their bulk equivalents, in two-dimensional (2D) layered materials, charge carriers are confined across thickness and are empowered to move across the planes. The features of 2D structures, such as quantum confinement, high absorption coefficient, high surface-to-volume ratio, and tunable bandgap, make them an encouraging contestant in various fields such as electronics, energy storage, catalysis, etc. In this review, we provide a gentle introduction to the 2D family, then a brief description of transition metal dichalcogenides (TMDCs), mainly focusing on MoS$_2$, followed by the crystal structure and synthesis of MoS$_2$, and finally wet chemistry methods. Later on, applications of MoS$_2$ in dye-sensitized, organic, and perovskite solar cells are discussed. MoS$_2$ has impressive optoelectronic properties; due to the fact of its tunable work function, it can be used as a transport layer, buffer layer, and as an absorber layer in heterojunction solar cells. A power conversion efficiency (PCE) of 8.40% as an absorber and 13.3% as carrier transfer layer have been reported for MoS$_2$-based organic and perovskite solar cells, respectively. Moreover, MoS$_2$ is a potential replacement for the platinum counter electrode in dye-sensitized solar cells with a PCE of 7.50%. This review also highlights the incorporation of MoS$_2$ in silicon-based heterostructures where graphene/MoS$_2$/n-Si-based heterojunction solar cell devices exhibit a PCE of 11.1%.

**Keywords:** 2D materials; heterostructure solar cells; MoS$_2$; graphene

**1. Introduction**

The house of 2D layered materials [1] has gained appreciable attention over the last few years, starting with the first segregation of graphene from a bulk counterpart, i.e., graphite [2]. The disclosure of every new material leads to enthusiasm and mystery because of the contrasting properties of these 2D materials from their bulk counterparts. Moreover, the fascinating 2D library is increasing in size every year and attributes a surplus of 150 exotic materials that can easily be cleaved into sub-nanometer 2D monolayers [3–6]. These 2D materials [7] include transition metal dichalcogenides (TMDCs), e.g., WSe$_2$, MoS$_2$, WS$_2$, hexagonal boron nitride (h-BN), silicene (2D silicone), germanene (2D germanium), borophene (2D boron), and MXenes (2D carbides/nitrides) [8–11]. In Figure 1, a publication list of 2D materials charted by year depicts an intensified craze of probing TMDCs.
Waals forces [3]. The layered structure of 2D materials permits efficient electronic properties and conductivity is prevalent along with the layers than between the layers, normally three or four folds of magnitude [13–15]. The disclosure of graphene and its distinctive properties in 2004 [16] introduced scientific insurgency where afterward a large number of more layered materials were exfoliated in 2D structures in a combination of elements highlighted in Figure 2a.

Graphene protruded from the other 2D materials because of its quirky properties like exclusive electronic band structure, high transparency with 0 eV bandgap, and thermal conductivity (3000–5000 Wm\(^{-1}\)K\(^{-1}\)) [17]. These unique properties enabled graphene to be a significant applicant in place of indium tin oxide (ITO)—that is transparent conductive oxide (TCO) thoughtfully applied in liquid crystal displays and LEDs, etc. Indium Tin Oxide (ITO) lost its performance due to the fact of flexibility shortfall and insufficient indium [18].

However graphene is a semimetal with zero bandgap, and in this scenario, one can say that other 2D materials, particularly TMDCs, have what graphene does not: a bandgap range of 1.2 to 1.8 eV [19], which admirably corresponds to solar spectrum and analogs to ongoing industrial needs in photovoltaic, e.g., Si (1.1 eV), CdTe (1.5 eV) or GaAs (1.4 eV). The upcoming generations of nanoelectronics require a discourse of the enhancing desire of reducing the size of elements in the circuit but not the quality. Due to the usage of monoatomic thin layers of 2D materials and their fine quality, it is possible to control electrostatic conductivity more efficiently. Moreover, the charge carrier scattering is reduced in 2D materials as compared to their bulk counterpart, owing to the reduced number of dangling bonds [20]. Two-dimensional materials are functional in electrochemistry having a high surface-to-volume ratio [21].

The sinking compact diameter of layered 2D materials would result in reduced volume, trimmed mass, and eventually the low cost of several devices in many different fields. Layered 2D materials have numerous applications in various domains based on their optoelectric character like in solar cells, photonics, protective light-absorbing layers, spintronics, conductive displays, and valleytronics, etc. [22,23]. As, vigorous attention has been paid to graphene from last many years and many review articles are available in literature so here we directly jump to layered TMDCs in this review article, detailing MoS\(_2\) and its incorporation in solar cell devices.
2. Transition Metal Dichalcogenides (TMDCs)

Layered 2D transition metal dichalcogenides contain a prodigious number of crystals and are represented by the general formula of MX2 where M is a transition metal from groups IV B, V B, VI B, VII B (Ti, Zr, Hf, V, Nb, Ta, Mo, W, Tc, Re) and X is a chalcogen element from group VI A (S, Se, Te) [4,24,25]. Figure 2b shows the general classification of 2D family. Depending upon the layer number, elemental conjunction, and presence or absence of dopant, TMDs exhibit a bandgap ranging from 0 to 2 eV, unlike the pure graphene which is a semimetal with 0 eV bandgap [21,23,26].

Transition Metal Dichalcogenides (TMDCs) are metals, semimetals, semiconductors, insulators, and superconductors conditioning on the elemental composition and structural layout as shown in Figure 2c. Layered TMDCs are leading successors of graphene and they are transparent, flexible, and as thin as graphene [27]. Apart from sharing comparability of bandgap, on/off ratio, and charge carrier mobility to that of ever-present silicon, TMDCs can also be stacked on to the flexible substrate and can bear stress and strain consents of flexible supports [28,29]. Among TMDCs, in this presented review, the ruling material is MoS2 because of its popularity based on the captivating properties.

**Crystalline Structure of MoS2**

In each layer of TMDCs (MX2) [30], the atomic layer of transition metal (M) is sandwiched between two atomic layers of chalcogens (X) as depicted in Figure 2d. In an MX2 monolayer, a covalent bond is formed by coordination of d orbital of M and p orbital of X atoms. Every individual layer is clenched by delicate Van der Waals forces. Considerably, all the approachable orbitals are tangled...
in intralayer bonding, in this scenario, only the high energy anti-bonding orbitals would be left behind for inter-layer bonding, accompanied with the absence of dangling bonds [31]. Because of weak Van der Waals forces between each layer, bulk TMDCs can be exfoliated into monolayers by chemical, mechanical, or electrochemical exfoliation methods. On account of the quantum confinement effect and surface properties, there are various properties observed in monolayer TMDCs which are not observed in their bulk counterparts. Layer dependent properties change when the thickness is being changed. The bandgap of TMDCs converts from indirect to direct: For example monolayer TMDCs, like MoS$_2$ (1.8 eV), MoSe$_2$ (1.5 eV), (2H)-MoTe$_2$ (1.1 eV), WS$_2$ (2.1 eV), and WSe$_2$ (1.7 eV), display direct bandgap, though their bulk counterparts show indirect bandgap accompanying smaller energies [26,32].

MoX$_2$ can formulate three types of crystal structures based upon the atomic stacking geography, trigonal prismatic (2H) phase, an octahedral (1T) phase, and rhombohedral (3R) phase [33,34]. In the 2H MoX$_2$ phase, every Mo atom prismatically collaborates to six neighboring S atoms and in the 1T-MoX$_2$ phase, the nearby six S atoms exhibit a distorted octahedron, circling one Mo atom. The 2H phase is thermodynamically stable and the 1T phase is metastable. The more inspiring thing is the interconversion of these two phases by intralayer atomic drift. According to these conditions by Li and K intercalation, 2H-MoS$_2$ can be transformed into the 1T-MoS$_2$ phase [35]. Therefore, the IT-MoS$_2$ phase is thermodynamically unstable, it converts back to the stable trigonal prismatic 2H-MoS$_2$ phase at room temperature. Both of these phases reveal contrasting electronic effects like the 1T-MoS$_2$ phase shows metallic [36] properties, whereas the 2H-MoS$_2$ phase represents semiconducting behavior and 1T-MoS$_2$ phase seems to be a more zestful catalyst for hydrogen evolution as compared to 2H-MoS$_2$ semiconducting phase. The 1T-MoS$_2$ phase shows metallic properties, whereas the 2H-MoS$_2$ phase represents semiconducting behavior which is important for optoelectronic devices [37].

Raman spectroscopy comfortably spots 1T and 2H phases. The $A_{1g}$ and $E_{2g}$ vibrational modes of the 1T-MoS$_2$ phase and 2H-MoS$_2$ phase have shown at ~380 and ~410, respectively. The 1T-MoS$_2$ phase displays several vibrational modes, because of their symmetric dissimilarities, classified as $j_1$ (~160 cm$^{-1}$), $j_2$ (~230 cm$^{-1}$), and $j_3$ (~330 cm$^{-1}$); no such vibrational modes were observed in case of 2H-MoS$_2$ phase [38,39]. It is not facile to acquire exact quantitative scrutiny of phase format from Raman spectroscopy singly because of the feeble Raman response of these vibrational modes. X-ray photoelectron spectroscopy (XPS) is an auxiliary technique to provide a significant quantitative analysis of 1T and 2H-MoS$_2$ phases. For pure 1T-MoS$_2$, the Mo 3d zone exhibits peaks at ~228.1 eV and at ~231.1 eV which are slightly at lower binding energies than those disclosed for the pure 2H-MoS$_2$ phase (~229.5 and ~232.0 eV) [40]. Raman spectroscopy is also helpful for locating the number of layers in TMDCs [41,42].

Numerous electronic properties of TMDCs emerge by stuffing the non-bonding d-bands, exhibiting metallic behavior when the orbitals are partially inhabited, and they show semiconducting properties when the orbitals are completely filled [43]. Chalcogen atoms have a slight impact on the electronic structure as compared to that of metal atoms, still, it is noticed that the bandgap decreases due to the broadening of d-bands by raising the atomic number of chalcogen atoms [44].

### 3. Synthesis of Two-Dimensional Materials

Two-dimensional materials are elucidated as a set of untied layered nanosheets, disclosing an elevated ratio of lateral size (from tens of nanometers to tens of microns) to thickness (from a few angstroms to a few nanometers) [11]. Graphene, exhibiting a single carbon layer of the honeycomb-like lattice structure, is the most popular and papery 2D material [45]. Depending upon the anatomy and crystallographic configurations, 2D materials are synthesized in the past decennary [46,47]. There is no uncertainty that two-dimensional materials have captivated researchers and engineers in various fields due to the fact of their gigantic number of species, considerably their distinctive properties and their auspicious applications in several fields like optoelectronics, energy conversion, energy storage, and electronics, etc.
There are a number of methods for synthesis of 2D materials, as listed in Figure 3a, including: Hummer’s method [48], micromechanical cleavage [1,49,50], liquid exfoliation [51] assisted by ion intercalation [52–55] and mechanical force [47,56–59], oxidation assisted liquid exfoliation [17,49,60], chemical vapor deposition [61–65], wet chemical synthesis method [66–69], electrochemical exfoliation [70–74], ball milling [51,75], etching-assisted exfoliation etc. [76–78]. All these methods can be grouped in two major classes of top-down and bottom-up approaches.

Figure 3. (a) Classification of synthetic strategies for 2D materials. (b) A simplified schematic of the liquid phase and electrochemical exfoliation of layered bulk material into 2D nanosheets.

In contrast to the bottom-up approach, top-down synthetic methods exhibit appreciable superiorities. Top-down synthesis methods give scalable production of exfoliated two-dimensional materials in an inexpensive and uncomplicated manner due to the low priced and highly available layered precursor material. The top-down approach includes synthetic methods such as liquid exfoliation through ion intercalation and mechanical force, liquid exfoliation through oxidation, and etching-assisted exfoliation, etc. Top-down approach is only limited to the 2D materials, of which the parental bulk counterpart is a layered material; however, the bottom-up approach is somehow more versatile in principle. Besides, downsides of top-down approach are also there such as defects production, more time consumption, and utilization of high-risk chemicals. Chemical vapor deposition (CVD) and epitaxial growth include the chemical reaction of precursors at specified experimental conditions.

The bottom-up synthesis method is nearly applicable to the exfoliation of all types of ultrathin 2D materials. Both, CVD and epitaxial growth processes take place at high temperature and vacuum. Moreover, an extra transfer step is required to shift the products from the metal surface to the selected substrate. During the transfer process, the risk of impurities enhances and it costs much higher.

Until now, a tremendous bloodline of 2D materials has been recorded such as transition metal dichalcogenides (TMDCs), graphene, graphitic carbon nitride (g-C₃N₄), black phosphorene, graphene oxide (GO), reduced GO (rGO), hexagonal boron nitride (h-BN), oxides, MXene, etc. Superb qualities have been shown by TMDCs (e.g., Ta₂NiS₅, WS₂, Bi₃Te₃, NbSe₂, VSe₂, Sb₂Se₃, WSe₂, MoS₂, and Ta₂NiSe₅) other than graphene. Alongside graphene, MoS₂, has come to the light as a future
candidate for optoelectronic applications, exhibiting excellent performance due to the face of its direct bandgap, quantum confinement, and higher mobility. Now, researchers are more interested in other 2D materials to enhance properties, like MoS$_2$ and h-BN, beyond graphene to compensate for the drawbacks of graphene. Because of zero bandgap, graphene has lost its application in optoelectronic devices and field-effect transistors. In this article, we will discuss the most common synthesis methods of MoS$_2$, WS$_2$, and graphene.

3.1. Synthetic Strategies for Graphene: Graphene as a Beginner

Here, we discuss the synthesis of the very first 2D materials which further extend to other 2Ds. Graphene is almost $1 \times 10^6$ times more slimmer than a human hair and approximately two-hundred-fold more powerful than steel. Additionally, graphene [79] is a better conductor than copper. There are numerous methods for the synthesis of 2D materials [7,46,80–83]; most commonly, one of them is the micromechanical cleavage method [1,50,51]. Energy is required to exfoliate the layered material into nanosheets [50,84]. In this prevailing cleavage method, Scotch tape is used for exfoliating the layered bulk crystals into nanosheets. [85] The intention to apply the mechanical force through Scotch tape is to weaken the out of plane Van der Waals forces without shattering the in-plane strong covalent bonds within each layer, consequently taking off a single or few layers of 2D materials. In the conventional method, the bulk 2D material (e.g., graphite) is attached to the sticky part of the Scotch tape and then take it off into single or few layers by adhering it to another sticky surface [1,51]. This process is replicated again and again in order to obtain the suitable thickness of flakes. Then, in the transfer method, split flakes on the Scotch tape are attached to the suitable substrate and peeled off from Scotch tape, leaving behind a single or few layer nanosheets on the substrate [50].

First, Novoselov, Geim, and co-workers [1], in 2004, mechanically exfoliated graphite into graphene nanosheets [86,87] and received a Noble Prize in 2010 [88]. Later on, this technique was also being used for the exfoliation of other 2D materials particularly the TMDCs, e.g., TiS$_2$, MoTe$_2$, TaSe$_2$, MoSe$_2$, WS$_2$, TaS$_2$, WSe$_2$, ReS$_2$ [50,88], h-BN [1,89], and metal phosphorous trichalcogenides, etc. There are numerous benefits of micromechanical cleavage method worth nothing, such as its harmlessness, because there is no use of chemicals; ideal crystal grade; and clean and defect-free surfaces with large lateral sizes [90]. Despite all these advantages, some flaws hamper its practical applications. First, mass production is not possible. Second, the yield is low compared to solution-based synthesis techniques. Thirdly, there is no control over the size, thickness, and morphology of nanosheets. Because the entire process is carried out manually, this is why there is deprivation of precision and repeatability [91].

3.1.1. Liquid Exfoliation of Graphene

For the exfoliation of graphite into graphite oxide, there is an additional extensively used method, which is called liquid exfoliation, assisted by oxidation [60]. Benjamin Collins Brodie [92], a British chemist, is known to be the first researcher who disclosed the fascinating properties of graphite oxide in 1859 [92]. From then on, because of the captivating properties of graphene oxide (e.g., super strong, highly conductive, thinness, and its wide applicability in various fields), GO appeared as one of the famous 2D materials and welcomed by the researchers. According to Brodie’s method, a mixture of graphite and potassium chlorate (KClO$_3$), with the ratio of 1:3, was reacted with fuming HNO$_3$ for 3 to 4 days at 60°C. Staundenmaier [93] in 1898, upgraded Brodie’s work by replacing fuming HNO$_3$ with H$_2$SO$_4$ and used manifold KClO$_3$ [93]. But this method caused hazards because of the usage of KClO$_3$, which is the source of the persistent explosion, and also it is a time taking reaction that takes 4 days [94]. Then, Hofmann in 1937, almost after 40 years, used non-fuming HNO$_3$ for the synthesis of graphene instead of fuming HNO$_3$ and revealed one more novel method that is more applicable and uncomplicated because of no requirements of repetition of oxidation process by four times [95,96].

In 1958, the chemist Hummer and his coworkers [48] developed a method for the synthesis of graphene oxide, this method is still used extensively [48], called Hummer’s method. In Hummer’s method, KClO$_3$, being replaced by KMnO$_4$ to prevent continuous explosion and NaNO$_3$ replaced
fuming HNO\textsubscript{3} to prevent the production of fog acid. The fundamental principle behind this method is the utilization of an extremely powerful oxidizing agent to make sure the oxidation of graphite into graphite oxide. Frequently applied oxidizing agents are KMnO\textsubscript{4} and concentrated H\textsubscript{2}SO\textsubscript{4} due to the vigorous oxidizing power of ions such as SO\textsubscript{4}\textsuperscript{2-} and MnO\textsubscript{4}\textsuperscript{2-}. Nitric acid is an exemplary intercalation representative, which expands the interlayer spaces and, thus, assists the intercalation of oxidative agents into the host galleries.

Some additional oxidative agents also cause the exfoliation of graphite, following the same mechanism of exfoliation, afar from ordinary ones [97]. On the surface of each graphene layer, functional groups containing oxygen species are developed due to the oxidation of graphite, which can cause the outstanding expansion of interlayer spacing of the bulk crystal and consequently remarkably debilitate the Van der Waals forces between the adjoining layers [49–61]. With the successive sonication remedy, single-layer graphene nanosheets are produced by the exfoliation of expanded graphite oxide. This method is useful for the production of graphene oxide nanosheets [49,61,62]; however, it cannot be applied further for exfoliation of other 2D materials. Hummers’ method is good in the way to give the mass production of GO nanosheets in solution with a major disadvantage of using a powerful oxidizing agent. This method is not as safe as the sonication assisted liquid exfoliation method. Hummer’s method fabricates more oxygen quantity than Brodie’s method [98]. But still, there are some flaws in hummer’s method [99] i.e., the production of toxic gases like NO\textsubscript{2} and N\textsubscript{2}O\textsubscript{4} [95]. Marcano et al. [100] distinguished hummer’s method, modified hummer’s method [101,102], and improved hummer’s method for the synthesis of graphene nanosheets based on the degree of oxidation of end product [100,103–106].

Epoxy, carboxyl, and hydroxyl, oxygen-containing functional groups are being introduced on the surface of graphene oxide due to the oxidation [107]. The oxygen-containing functional groups can be partially eradicated from the surface by reduction of the oxygen-containing specie, graphene oxide, into reduced graphene oxide (rGO) nanosheets. There are numerous approaches for the reduction of GO nanosheets (e.g., reduction through chemical reaction by using reducing agents), photochemical reduction, reduction by electrochemical means, thermal annealing, and others [61,74,104,108–113]. GO as well as the rGO, show different electronic, physical and chemical properties in contrast to their bulk counterpart (pristine graphene). The most striking distinction is the superb electrical conductivity of graphene, while GO nanosheets are electrically insulator [114]. Even though, GO nanosheets reduced back to the rGO nanosheets, but the electrical conductivity was not comparable to the graphene obtained from CVD method or through mechanical exfoliation method. Furthermore, GO has functional groups on its surface, it is hydrophilic and admirably dispersible in water [115], whereas on the other side, graphene is hydrophobic [116]. Due to these distinguishing characteristics, GO and rGO are called derivatives of graphene, rather than just saying them, graphene. The electrical conductivity can be manipulated, to electrical conductor from insulator, by precisely adjusting the number of oxygen-containing functional groups on the surface of GO [107].

3.1.2. Electrochemical Exfoliation of Graphene

By moving forward from Scotch tape cleavage and liquid exfoliation method, electrochemical exfoliation is another method for exfoliation of graphite into its 2D morphology. The utilization of the suggested by Brodie, Staudenmaier, and Hummers is well known for mass production and low cost. However, these methods involve strong oxidants and acids which results in the emission of toxic gases and can also deteriorate the sp\textsuperscript{2} bonding in graphene. Moreover, these methods are time-consuming including the production of defects as well. Most recently, considerable attention has been paid to the electrochemical exfoliation method for the synthesis of graphene nanosheets. Electrochemical exfoliation is simple, greener, fast, scalable, and low-cost synthesis method and gives a product (graphene) with lesser defects and higher crystallinity. This method also allows the tuning of the degree of oxidation in the product. Table 1 briefly describes the efforts of different research groups for the synthesis of graphene nanosheets by the method of electrochemical exfoliation of graphite.
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Table 1. Strategies to synthesize graphene using a series of electrochemical exfoliation methods.

| Synthesis Strategy | Title of Paper | Specifications | Year of Publication | Author + Reference |
|--------------------|----------------|----------------|---------------------|--------------------|
| Electrochemical exfoliation | One-step ionic-liquid-assisted electrochemical synthesis of graphene sheets directly from graphite | 1-ethyl-3-methylimidazolium hexafluoro-phosphate (8mim + PF6) (ionic liquid IL) along with water used as an electrolyte. Two graphite rods were used as electrodes. Obtained graphene nanosheets (GNs) did not disperse in water but polar aprotic solvents. | 2008 | B.N. Liu et al. [117] |
| Electrochemical exfoliation | One-pot synthesis of fluorescent carbon nano-ribbons, nano-particles, and graphene by the exfoliation of graphite in ionic liquids | Synthesis of graphene sheets in a single vessel using graphite rod and platinum wire as electrodes and 1-methyl-3-butytrimidazolium tetrafluoro-borate (or 1-methyl-3-butytrimidazolium chloride) as an electrolyte in combination with water in varying ratios. | 2009 | L. et al. [118] |
| Electrochemical exfoliation | An electro-chemical route to graphene oxide | Expanded graphite used as anode and Pt wire as a counter electrode along with KOH as an electrolyte. The lateral size of the exfoliated graphene sheet was 30 μm. The transparent conducting film, containing these exfoliated graphene sheets, was found to be conductive but the yield was low. | 2011 | You et al. [119] |
| Electrochemical exfoliation | High-quality thin graphene films from fast electrochemical exfoliation | Highly oriented pyrolytic graphite (HOPG) used as a graphene source, grounded Pt wire used as a counter electrode, and H2SO4 used as the electrolyte. The lateral size of the graphene sheet was ~1.5 nm. | 2011 | Su et al. [120] |
| Electrochemical exfoliation | Synthesis of high-quality graphene through electro-chemical exfoliation of graphite in alkaline electrolyte | Graphite rod and platinum wire were used as electrodes along with alkaline electrolyte (KOH) in the electrochemical setup. Graphene is obtained with fewer defects, good quality, 1–4 layers, and with lateral size up to ~80 μm. | 2013 | Tripathi et al. [121] |
| Electrochemical exfoliation | Electrochemically exfolated graphene as solution-processable, highly conductive electrodes for organic electronics | H2SO4, graphite flakes, and platinum wire were used as an electrolyte, anode, and cathode respectively. The thickness of the obtained graphene was ~1.5 nm for bilayer and size of exfoliated graphene sheets was up to 5–10 μm. | 2013 | Parvez et al. [122] |
| Electrochemical exfoliation | Few-layer graphene obtained by electrochemical exfoliation of graphite cathode | A system of dimethyl sulfoxide (DMSO), NaCl, water, and thionin acetate was used as an electrolyte for exfoliation of graphite cathode. The thickness of the obtained graphene sheets was less. | 2013 | Zhou et al. [123] |
| Electrochemical exfoliation | Synthesis of graphene oxide nano-sheets by electrochemical exfoliation of graphite in cetyl-trimethylammonium bromide and its application for oxygen reduction | Cetyltrimethylammonium bromide (CTAB) used as electrolyte where-as graphite rod and Pt wire were used as electrodes. GO/CTAB suspension is tremendously stable in ambient conditions. The single-layer thickness of the obtained graphene is 2.5–4.5 nm. | 2014 | Kakaei and Hasanpour [124] |
| Electrochemical exfoliation | Role of peroxide ions in formation of graphene nanosheets by electrochemical exfoliation of graphite | A network of NaOH/H2O2/H2O was used to exfoliate graphite. High-quality graphene sheets with 3–4 layers are formed exhibiting a thickness of ~1–2 nm with a 95% yield. | 2014 | Rao et al. [125] |
| Electrochemical exfoliation | Exfoliation of graphite into graphene in aqueous solutions of inorganic salts | Inorganic salts such as NaH2SO4, K2SO4, and Na2SO4 used as electrolytes for the synthesis of graphene sheets. Graphene sheets showed vast lateral size, low oxidation level, and elevated yield of 85%. | 2014 | Parvez et al. [126] |
| Electrochemical exfoliation | Graphene synthesis via electrochemical exfoliation of graphite nanoplatelets in aqueous sulfuric acid | Utilized pressed-graphene nanoparticles (GNPs) used as anode and Pt wire as a cathode with 0.1M sulphuric acid as an electrolyte. Flakes size is more manageable | 2016 | Lin Li et al. [127] |
| Electrochemical exfoliation | Preparation of graphene sheets by electrochemical exfoliation of graphite in confined space and their application in transparent conductive films | In EECS (electrochemical exfoliation in confined space) nickel foam is used as a counter electrode while the working electrode is graphite rod covered with paraffin, with bottom opening, in an alkaline electrolyte (10 mol/L NaOH). Paraffin helps to control the extravagant exfoliation of graphene. Graphene rooted conductive sheets can replace indium tin oxide. | 2017 | Hui Wang et al. [128] |
| Synthesis Strategy                  | Title of Paper                                                                 | Specifications                                                                                                                                                                                                 | Year of Publication | Author(s) and Reference |
|------------------------------------|-------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------|-------------------------|
| Electrochemical exfoliation        | Electrochemical exfoliation synthesis of graphene                            | Graphite rod and Pt wire placed vertically in the electrochemical cell along with protonic acid as an electrolyte. In the vertical configuration, exfoliation is much better organized and graphene synthesized with better quality as well as quantity. | 2017                | J. Liu and Theses [127] |
| Electrochemical exfoliation        | Electrochemical exfoliation of graphite into graphene for flexible supercapacitor application | Graphite rod and Pt used as electrodes, 0.1M potassium sulfate used as the electrolyte. The size of graphene nanosheets is in between of 433 nm to 5.07 \( \mu \)m. | 2018                | Singh and Tripathi. [128] |
| Electrochemical Exfoliation        | A facile synthesis of graphene oxide (GO) and reduced graphene oxide (rGO) by electro-chemical exfoliation of battery electrode | GO being synthesized by using ionic specie as an electrolyte, graphite rods as electrodes, and regulated DC power supply. GO being reduced to rGO using ascorbic acid, i.e., environmentally benign reducing agent. | 2019                | Vartak et al. [129]     |
| Electrochemical exfoliation        | Controlled synthesis of graphene via electrochemical route and its use as efficient metal-free catalyst for oxygen reduction | \((\text{NH}_4)_2\text{SO}_4\) used as electrolyte whereas Pt and graphite substrate served as the two electrodes in electrochemical setup. High standard graphene with governable layer number was fabricated using cost-effective precursors. | 2019                | Komba et al. [130]      |
| Electrochemical exfoliation        | A single-step strategy to fabricate graphene fibers via electrochemical exfoliation for micro-supercapacitor applications | The simplistic, economical top-down synthesis method is used to fabricate porous, fiber-like graphene. Graphene fibers showed high specific capacitance, high electrochemical performance because of porous structure and fine electronic conductivity. | 2019                | He et al. [131]          |
3.2. Synthetic Strategies for TMDCs

In 2004, after the successful exfoliation of graphene from graphite, by Novoselov and his coworkers [1], a series of experiments were performed on TMDCs, more specifically on MoS$_2$ [132]. Nevertheless, TMDCs traveled the journey of seven years to step out of the umbra of famous graphene to certify their identification. To formulate their various 2D forms, a variety of exfoliation methods has been originated to split the piled-up layers in bulk TMDCs [133–135]. The basic drive behind the exfoliation of liquids is to provide a suitable amount of energy to the liquids to conquer the van der Waals interactions between the layers. Synthesis methods including micromechanical cleavage, liquid exfoliation, intercalation, etc., are classified under top-down synthesis methods. Top-down and bottom-up approaches have been discussed in Section 3.

The strong in-plane bonding and relatively delicate interlayer bonding enables the layered 2D materials to be separated into isolated, atomically slim nanosheets, where nano advert to the extent of thickness [57]. Micromechanical cleavage [49,50], discussed in Section 3.1, is the foremost successful method to spare 2D layered materials into the individual layers from their bulk counterparts [88,136]. No doubt, the micromechanical cleavage method [49] gives fine quality mono and few layers with the least defects, but this method is restricted due to low yield and deficient thickness control. To overcome this problem, one popular method is the liquid phase exfoliation through the solvent, sonication, and with/without ion intercalation strategy.

3.2.1. Liquid Phase Exfoliation of TMDCs

Liquid phase exfoliation is the most extensively applied synthesis method to fabricate the nanosheets of TMDCs [137–139]. The basic mechanism behind liquid exfoliation involves three steps. Firstly, the dissolution of the respective bulk TMDCs in the suitable solvent. Secondly, the exfoliation of the bulk counterpart into nanosheets by sonication. However, surfactants are added as a stabilizing agent [140,141]. Third and the least one, separation of individual sheets and centrifugation. Figure 3b is the simple schematic demonstration of liquid phase exfoliation through sonication and ion intercalation and exfoliation through the electrochemical method to obtain the nanosheets at the end as a major product. A wide domain of other 2D materials can also be synthesized such as graphene [142–145], boron nitride [146,147] and phosphorene [148,149] by this method. Depending on the energy source implemented for exfoliation and dispersion of nanosheets, the liquid phase exfoliation method has been divided into two categories, i.e., liquid exfoliation through sonication [150] and liquid exfoliation through sheer force.

In the liquid phase, bulk TMDCs can be converted into nanosheets by sonication [151,152]. Following the dispersion of bulk powder in the required solvent (e.g., N-methyl-2-pyrrolidone, NMP) for exfoliation, a probe sonicator, a bath sonicator or the combination of both of them, is used. In ultrasonicated dispersions, because of cavitation bubbles’ collapse, microjets and shock waves are produced [153–155], which causes the exfoliation of bulk crystal into nanosheets in the liquid phase [156]. To get the systemized exfoliation of TMDs, the critical aspect is the comparable surface energies of bulk TMDs crystal and the solvent being used. The dispersion, after sonication, treated with centrifugation for about an hour at 500–1500 rpm [157]. Ultimately, the supernatant, containing mono and few-layer nanosheets of MX$_2$, collected from centrifuged dispersion. This obtained dispersion of nanosheets is suitable for a number of techniques such as electrodeposition, spray coating, spin coating, vacuum filtration, etc. [158,159].

From all around the world, there are a large number of research groups, including the Ajayan group [86] and Coleman group [159], they applied liquid phase exfoliation in different liquid media and synthesized almost all 2D materials [86,156,157]. In a guideline article, the method of exfoliation, characterization, and processing of 2D materials has been discussed by Backes, Coleman, and coworkers [160]. Additionally, they facilitated the research world with a tutorial video as well [161]. Liquid phase exfoliation through sonication has an energetic group with wealthy literature and in recent years the discipline has been massively reviewed.
Via a range of experiments, Coleman et al. [157] proposed the optimized solvents for MoS$_2$ and WS$_2$. Different 2D materials have different surface energies, and consequently, different solvents are required to form the stable dispersions of different materials [162,163]. Precisely, the surface energies of MoS$_2$, h-BN, and graphene are 46–65 mJ cm$^{-2}$, 44–66 mJ cm$^{-2}$, and 70 mJ cm$^{-2}$ [157,164]. Many good solvents like NMP and DMF (N,N-dimethylformamide) have high boiling points and the leftover solvent can damage the 2D materials. That’s why, the solvents having low boiling points would be preferred [165,166]. There is a vast collection of solvents in literature (e.g., 1-butyl-3-methylimidazolium chloride ionic, tetrahydrofuran (THF), methanol, acetone, and ethanol, etc.), to make nanosheet’s dispersions of MoS$_2$ [167]. For exfoliation of transition metal dichalcogenides by sonication in water or the solvents having low boiling points, a diversity of ionic surfactants [168], polymers [169–171], and nonionic surfactants [172,173] have been practiced in literature.

Although, an appreciable amount of 2D materials can be achieved through sonication assisted liquid exfoliation as compared to micromechanical cleavage method, still, this method cannot cover the requirements for industrial exertion. To boost up the mass production of 2D materials, the exfoliation of 2D materials was supported by shear force in liquid media [174,175]. A method raised by Paton et al. [176], shear force assisted exfoliation in the liquid phase, applying shear force for exfoliation of 2D materials accompanied by intense shear rates. Coleman and his coworkers [176], implemented a rotor-stator mixer with a high shear rate to promote the production rate of graphene thin flakes [176]. In the liquid, carrying the bulk 2D crystal, a mixer can kindle the intense shear rates under strong rotation speed [50]. The shear forces under the influence of intense shear rates prompted the exfoliation of bulk 2D materials in the liquid phase. The utilization of suitable solvents and polymers can prune the energy tariff of the exfoliation method as well as provide the stability to nanosheets. This method further implemented for the exfoliation of graphene, h-BN, and TMDs [177,178].

Exfoliation through ion intercalation in liquid media is an additional example of the top-down synthesis method. The core objective of this method is to inject the cation ions (e.g., Cu$^{2+}$, Na$^+$, K$^+$, or Li$^+$ ions), in the host material galleries, having a small ionic radius to form the ion-expanded compound. Conventionally, reducing agents and electron donor species could be injected directly in between the layers of bulk 2D materials [179]. Ion intercalation causes the expansion of the layers in host 2D material and deliberate the van der Waals interlinkages between the adjoining layers in the bulk material [122,180]. The ion injected compound can be comfortably exfoliated into mono or few layers nanosheets under specific conditions, i.e., specific solvent, sonication time, etc. For the above half-century almost, intercalation of alkali metal ions have been investigated [181]. The key benefit of alkali metals is their smaller size, which helps to get into the host galleries. The addition of alkali metal-expanded layered material into water causes the hydrogen bubble formation in the liquid, which causes further expansion of layers and helps exfoliation of the bulk crystal. The most frequently used alkali metal is Li, using organometallic compounds (e.g., n-butyllithium) for intercalation, which possesses the smallest size and exhibits higher reactivity as compared to the other alkali metals.

A large number of layered materials can be exfoliated using Li$^+$ intercalation, e.g., graphene, h-BN, TMDs, etc. [35].

Back to the 1980s, Morrison, and co-workers [182] exfoliated bulk MoS$_2$ crystal into monolayered MoS$_2$ nanosheets, using n-butyllithium being intercalator, by Li intercalation method in liquid media. Large compounds, like n-butyllithium (n-BuLi) including tert-butyllithium (t-BuLi) exhibit more effective exfoliation as compared to smaller compounds such as methyllithium (MeLi) [183,184]. In the conventional process, 2D bulk materials, in the environment of Ar or N$_2$, introduced into the n-butyllithium solution for some days. High temperature or stirring is being frequently used to enhance the efficiency of the intercalation process. By injecting lithium ions (Li$^+$) between the layers, exfoliation of Li$_x$MoS$_2$ takes place, through hydrolysis, into monolayers. At the hydrolysis stage, ultrasonication being applied to enhance the hydroxyl group diffusion and to improve the exfoliation efficiency [185]. Eda et al. [186] used n-BuLi to exfoliate MoS$_2$ with 50% semiconducting 2H-MoS$_2$ phase and 50% metallic 1T MoS$_2$ phase. Zheng et al. [54] used the ion intercalation process...
in combination with the hydrothermal method to synthesize the large area MoS$_2$ nanosheets [54]. Other than $n$-butyllithium, some other compounds (LiBH$_4$) also proved efficient intercalators for 2D nanomaterials [187]. Pumera and coworkers [188] compared Li intercalation process efficiency and transitions between 1T and 2H phases of MoSe$_2$, MoS$_2$, WSe$_2$, and WS$_2$. Moreover, with the help of ultrasonication [189] and microwave-induced intercalation [190], the efficiency of the Li intercalation process can be improved. Liquid exfoliation through the ion intercalation process has been applied to synthesize various 2D nanomaterials like Cu$_2$WS$_4$, MoSe$_2$, WS$_2$, MoS$_2$, ReS$_2$, and TiS$_2$ [54,191,192].

Limitations to the Li intercalation process are there as well. Usage of organometallic compounds, which are reactive to air and moisture and are explosive, N$_2$ or Ar glove box is required. Additionally, long reaction time, insufficient monolayer yield, deprivation of semiconducting phase, the inadequacy of controllability, and lateral sizes of exfoliated sheets are in the sub-micron region, are drawbacks of Li intercalation process [184,193]. Consequently, some intercalators, other than lithium, being used by scientists to improve the exfoliation efficiency of TMDCs [55,194–196].

3.2.2. Electrochemical Exfoliation of MoS$_2$/WS$_2$

To produce the solution-processable and large scale exfoliated MoS$_2$ by chemical means [197–199], enormous attempts have been committed. Among those attempts, the electrochemical exfoliation method is one. The utilization of the electrochemical approach assists the exfoliation process for the mass production of two-dimensional layered materials. Table 2 compiles the research efforts from 2010 to 2018 in the electrochemical exfoliation of MoS$_2$ from bulk to its nanosheets. Zeng et al. [199] used MoS$_2$ bulk material as cathode and lithium foil as a counter electrode in the electrochemical setup. Lithium ions get incorporated between the layers and cause exfoliation. In the course of intercalation of lithium ions, every Li atom also inserts one electron with it in host layered material. The intercalation of a large number of lithium ions causes massive injection of electrons in MoS$_2$ layered material (host material) which gives rise to the undesired transition of the 2H-semiconducting phase into 1T-metallic phase. You et al. [200] exfoliated MoS$_2$ by using H$_2$SO$_4$ as electrolyte and platinum as a counter electrode. Later, the aforementioned group modified the exfoliation method by incorporating SO$_4^{2−}$ ions at neutral pH value and resulted in the generation of MoS$_2$ nanosheets with large lateral size and having a lower oxidation level as well [201]. There are various constraints and challenges, in the electrochemical exfoliation method, which have to be taken into consideration while talking about two-dimensional materials except for graphene. Major restriction is the need of conductive material, so the method is restricted to only conductors and semiconductor materials. Moreover, there are some other parameters of study like material should be strong enough to resist the chemical changes due to anodic or cathodic oxidation and should have stability in ambient circumstances as well. Only MoS$_2$, Bi$_2$Se$_3$, graphene, black phosphorous, and Bi$_2$Te$_3$ have been successfully exfoliated in aqueous electrolyte by electrochemical means because this method is in premature stage for 2D materials other than graphene and a lot of work must be done in this area [202].
Table 2. Electrochemical exfoliation methods for the synthesis of MoS₂/WS₂ nanosheets.

| Synthesis Strategy | Title of Paper | Specifications | Year of Publication | Author + Reference |
|--------------------|----------------|----------------|--------------------|--------------------|
| Electrochemical exfoliation | Single-layer semiconducting nanosheets: high-yield preparation and device fabrication | The multi-layered bulk material (MoS₂, WS₂, Graphene, etc.) was used as a cathode in the electrochemical cell while lithium foil being used as an anode. LiPF₆ used as an electrolyte. Monolayer yield is 92% in this method for MoS₂. | 2011 | Zeng et al. [199] |
| Electrochemical exfoliation | Large-area atomically thin mos₂ nanosheets prepared using electrochemical exfoliation | Na₂SO₄ being used as an electrolyte along with a pure single crystal of MoS₂ as a working electrode and Pt wire as a counter electrode. This synthesis method ended up giving the yield of MoS₂ monolayers up to 5–9% with 50 µm lateral size of sheets, little oxidation and acceptable quality. | 2014 | Liu et al. [201] |
| Electrochemical exfoliation | Electrochemical exfoliation of mos₂ electrogeneration crystal for hydrogen | Pt foil and MoS₂ crystal being used as electrodes in electrochemical setup including K₂SO₄ as the electrolyte. The obtained lateral size of MoS₂ nanosheets was 100-200 nm with 15-20 layers. | 2018 | Ambrosi & Pumera [71] |
| Electrochemical exfoliation | Solution-processable 2d semiconductors for high-performance large-area electronics | In electrochemical setup, MoS₂ crystal being intercalated by THAB (tetraheptylammonium bromide). After intercalation, the enlarged MoS₂ crystal was sonicated in PVP/DMF (poly-vinylpyrrolidone solution in dimethylformamide). PVP provided stability to the monolayers of MoS₂ from stacking back. Obtained nanosheets have had a thickness of 3.8 nm with a lateral size of 0.5–2 µm. | 2018 | Lin et al. [203] |
| Electrochemical exfoliation | Advanced composite 2d energy materials by simultaneous anodic and cathodic exfoliation | Single MoS₂ crystal sank in TBA⁺ in electrochemical setup. Firstly, the bulk crystal was immersed in acetonitrile but later acetonitrile replaced by TBA⁺ for better expansion. Cathodic exfoliation gave MoS₂ monolayers with great crystallinity and no defects were observed as well. | 2018 | Li et al. [204] |
The sinking compact diameter of layered 2D materials would result in reduced volume, trimmed mass, and eventually the low cost of several devices in many different fields. Layered 2D materials have numerous applications in various domains based on their optoelectric character like in solar cells, photonics, protective light-absorbing layers, spintronics, conductive displays, and valleytronics, etc. [22,23]. As, vigorous attention has been paid to graphene from last many years and many review articles are available in literature so here we directly jump to layered TMDCs in this review article, detailing MoS$_2$ and its incorporation in solar cell devices.

4. Applications of MoS$_2$ in Opto-Electric Devices

Among 2D materials, graphene, a semimetal with zero bandgap, was the first to be tremendously used in various applications of science and technology [205]. However, due to the zero bandgap, graphene has restricted its applications in optoelectronics and field-effect transistors. In a very short time, following the disclosure of graphene, special attention was being paid to other 2D materials, e.g., h-BN, phosphorene and TMDCs, etc. [11,206]. Transition metal dichalcogenides (TMDCs) have diversity in terms of their properties like they exhibit excellent optical, mechanical, and electronic properties. As we are interested in optoelectronic properties for photovoltaic applications, the main focus is on optical and electronic properties [207]. In terms of optical properties, they give superb photoabsorption in visible and near IR range (absorption co-efficient is $10^5$–$10^6$ cm$^{-1}$). Transition metal dichalcogenides (TMDCs) have a tunable bandgap, vary while reducing the thickness, show transition from indirect to direct bandgap, exhibit powerful light-matter interactions and due to the quantum confinement effect, they show intense photoluminescence. The direct bandgap, high mobility (50 cm$^2$/V s), and strong interaction with light give monolayer TMDCs a big breakthrough in applications of photovoltaics [208].

4.1. MoS$_2$ as Absorber Material in Solar Cells

Transition metal dichalcogenides (TMDCs), more specifically MoS$_2$, with a 2H crystal system, are largely acceptable in PV (photo voltaic) applications [209]. The bandgap of TMDCs varies from 1.0 to 2.0 eV, which is comparable with the solar spectrum, in correspondence with other famous solar cell semiconductors like Si (1.1 eV), CdTe (1.5 eV) and GaAs (1.4 eV) [210]. It has been stated that in the thickness of 1 nm, 2D TMDCs can show 5–10% absorption of incident light per unit volume and can attain higher absorption efficiency of sunlight, compared to the frequently used materials like Si and GaAs as light absorbers. The amount of light absorbed by the monolayer of TMDCs is comparable to the amount of light being absorbed by 50 nm thick Si layer and gives higher photocurrent values (2.0–4.5 mA/cm$^2$) [211].

4.2. MoS$_2$ as a Counter Electrode in Dye-Sensitized Solar Cells

In dye-sensitized solar cells, the counter electrode plays an important role by transferring electrons through an external circuit to tri-iodide ions for the reduction process. The photoelectrochemical process in DSSCs (Dye-Sensitized Solar Cells) strongly influenced by the electrocatalytic effect of the counter electrode [212]. MoS$_2$ is a replacement in DSSCs as a counter electrode as compared to traditionally used high-priced Pt electrode [213–215]. MoS$_2$ used in three contrasting structural architectures, i.e., MoS$_2$ nanoparticles, few-layered MoS$_2$, multi-layered MoS$_2$ as a counter electrode by Lei et al. [216]. The devices containing these MoS$_2$ morphologies exhibit the photon conversion efficiency of 2.92% for ML-MoS$_2$, 5.41% for MoS$_2$-NPs, 1.74% for FL-MoS$_2$. MoS$_2$ implanted with graphene flakes also used as a counter electrode by Lin et al. [217] and power conversion efficiency (PCE) achieved was 6.07%. MoS$_2$ gives a fast reduction process of triiodide ion and Graphene flakes, being highly conductive, give speedy charge transfer. Liu et al. [218] used nanocomposite of MoS$_2$/rGO as a counter electrode and reported PCE 6.04%.
4.3. MoS$_2$ as a Diverse Role Material in Organic Solar Cells

Organic solar cells have numerous remarkable properties in particular lightweight, flexibility, facile synthesis and solution processability, etc. In typical organic solar cell layout, a blend of photoactive material with electron donor and electron acceptor material is present. Mostly used hole transport layer is a blend of PEDOT: PSS (Poly (3,4-ethylenedioxythiophene): poly(styrene sulfonate) in organic solar cells. Graphene, TMDCs, and carbon nanotubes were investigated as a hole extraction layer in place of PEDOT: PSS blend [219].

MoS$_2$ can be used as a hole transport layer (HTL), electron transport layer (ETL), the buffer layer, and as an interfacial layer in organic solar cells [220].

Gu et al. [221] reported MoS$_2$ as a HTL instead of PEDOT:PSS in (poly(4,8-bis[(2-ethylhexyl)oxy]benzo-[1,2-b:4,5-b]dithiophene-2,6-diyl)][3-fluoro-2-[2-(ethylhexyl)-carbonyl]thieno[3,4-b]thiophenediyl]) PTB7: PC71BM based solar cell and also in (3-alkylthiophenes) P3HT: PC71BM ([6,6]-Phenyl C71 butyric acid methyl ester) based organic solar cells which exhibited PCE of 8.11% and 4.02%, respectively. In PTB7: PC71BM-based solar cells, PCE changes from 6.97% to 8.11% by changing the number of layers of MoS$_2$, showing the dependence of PCE on different number of layers of MoS$_2$. In PTB7: PC71BM-based monolayer MoS$_2$ solar cell, VOC of 0.69 V, fill factor of 64%, JSC of 15.78 mA/cm$^2$ and PCE of 6.97% obtained.

MoS$_2$ is also used as an anode buffer layer by Li et al. [222] in organic solar cells to prevent the current leakage between bare ITO and PC61BM and showed the PCE of 3.9%. PCE of 2.14% achieved in organic solar cells consisting of bare ITO without a buffer layer. A nanocomposite of PEDOT: PSS/MoS$_2$ can also be used as a hole extraction layer in P3HT: PCBM ([6,6]-phenyl-C61-butyric acid methyl ester) based organic solar cells giving PCE value of 3.74% [223]. Yang et al. [224] used MoS$_2$ as a hole withdrawing layer in the organic solar cell. In respective organic solar cell PTB7: PC71BM used as an active layer, PFN poly[(9,9-bis(3’-(N,N-dimethylamino)-propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] as the electron transport layer and oxygen-containing MoS$_2$ was used as hole withdrawal layer produced by UV–ozone treatment. As compared to PEDOT: PSS, both, MoS$_2$ nanosheets and oxygen containing MoS$_2$ nanosheets exhibited surpassing optical transparency in the region of 400–900 nm with PCE of 4.99%.

Hole transport material demands profound work function and there must be the material of low work function for electron extraction in organic solar cells, due to this reason, graphene and its derivatives can be used as both electron and hole extraction layers in the organic solar cell because of their tunability of work function. Yun et al. [225] used MoS$_2$ as an electron extraction layer and hole withdrawal layer as well. P-type doped MoS$_2$ used as a hole withdrawal layer and the n-type doped layer was used as an electron extraction layer. Photon conversion efficiency increased from 2.8% to 3.4% in organic solar cells containing p-type doped MoS$_2$ as a hole extraction layer.

MoS$_2$ used as an interfacial layer and silver nanowires along with MoS$_2$ were used as a transparent electrode by Hu et al. [226] AgNW-MoS$_2$ as a transparent electrode shows 93.1% transparency at 550 nm and gives lower values of sheet resistance (9.8 $\Omega$/sq). MoS$_2$ in the AgNW-MoS$_2$ composite electrode helps to improve the environmental reliability and provides better resistance against oxidation and moisture as compared to the AgNW electrode alone. PBDTTT-C-T: PC70BM based organic solar cell gives PCE of 8.72% by using the anode of p-MoS$_2$ nanosheets/Ag for hole extraction and cathode of AgNWs-MoS$_2$ nanosheets/n-MoS$_2$ nanosheets for electron extraction. General cell configuration, in this case, is glass/AgNW-MoS$_2$/n-MoS$_2$/PBDTTT-C-T: PC70BM/p-MoS$_2$/Ag being sketched in Figure 4a. MoS$_2$ in combination with MoO$_3$ and MoS$_2$ with Au nanoparticles were also used as hole extraction layers in organic solar cells by Qin et al. [227] and Yang et al. [228] respectively. Chuang et al. [229] used nanosheets of MoS$_2$ along with Au nanoparticles as an electron extraction layer and obtained PCE of 4.91%.
The generic formula of perovskite solar cells is ABX₃. Most commonly in organometallic halide perovskites solar cells, A is CH₃NH₃⁺ and B is Pb. Whereas X is an anion which is a halogen (Cl, Br, I) [232]. For separation and collection of generated charges, electron and hole extraction layers are inserted between the active layer and electrodes. Spiro-OMeTAD (2,2',7,7'-tetrakis(N,N-di-p-methoxyphenyl-amine))9,9'-spirobi fluorenes) mostly used as hole transport material in perovskite solar cells because HOMO of Spiro-OMeTAD and valence band maxima of CH₃NH₃PbI₃ has energy levels at 5.03 eV and 5.04 eV respectively. Spiro-OMeTAD productively conduct holes from the active layer (CH₃NH₃PbI₃) to the anode, but it is not cost-effective. That is why a number of other materials were used in its place in perovskite solar cells such as poly(3-hexylthiophene) P3HT [232,233], graphene oxide (GO) [234], poly(3,4-ethylene dioxythiophene) polystyrene sulfonate (PEDOT:PSS) [235], reduced graphene oxide (rGO) [236,237], copper(l) iodide (CuI) [238] and MoS₂ [239], etc.

Kim et al. [240] deliberated the hole transfer characteristic of MoS₂. The work function of MoS₂ (4.95 eV) is in the same league as PEDOT: PSS (5.25 eV), consequently, MoS₂ can also be used as a hole transfer layer in perovskite solar cells. Kim et al. [240] reported a PCE of 9.53% for MoS₂-based devices. Capasso et al. [241] used MoS₂ as HEL in perovskite solar cell that gives PCE of 3.95% as compared to the PCE of 3.1% obtained using spiro-OMeTAD (3.1%). MoS₂ monolayer incorporated in perovskite solar cells to give protection and hole transportation. Furthermore, few layers of MoS₂ (3 nm thick) nanosheets can be used to protect the short circuit between the two electrodes and to conduct the holes from the active layer (perovskite) to spiro-OMeTAD. Power conversion efficiency (PCE) of perovskite solar cell increases to 16.47%, by mixing MoS₂ with PEDOT: PSS and used as a hole transfer layer, as compared to PCE of (14.69%) obtained by using PEDOT: PSS solely. Capasso et al. [242] revealed that in the configuration of glass/FTO/compact-TiO₂/mesoporous-TiO₂/CH₃NH₃PbI₃/MoS₂/Spiro-OMeTAD/Au solar cell, PCE of 13.3% can be obtained with higher stability.

Wang et al. [230] used MoS₂ and GO in perovskite solar cell and cell configuration was ITO/PEDOT: PSS/GO/perovskite/PCBM/MoS₂/Ag as shown in Figure 4b. Using MAPbI₃ as an active layer, PCE achieved was 19.14%, increased from 14.15% with VOC of 1.135 V, increased from 0.962 V. Dasgupta et al. [239] used p-type doped MoS₂ in perovskite solar cells containing MAPbI₃ and reported...
6.01% PCE. Huang et al. [243] used MoS\(_2\) as hole transport material in perovskites and achieved PCE of 15.4% and by using WS\(_2\) as HTL, PCE of 20% achieved. The higher photon conversion efficiency of TMDCs is due to the well-aligned valence band of specific TMDC and perovskite material, lower value of series resistance, and higher shunt resistance. Kakavelakis et al. [244] incorporated MoS\(_2\) as an interlayer between active layers (perovskite material) and hole transport layer (PTAA) and enhance the efficiency of perovskite solar cells by 6% as compared to the perovskite solar cells without MoS\(_2\). Kohnhepoushi et al. [245] also used MoS\(_2\) as a hole withdrawal layer in MAPbI\(_3\) containing perovskite solar cells and reported PCE of 20.53%.

Ahmed et al. [246] used a composite of MoS\(_2\) with TiO\(_2\) as an electron extraction layer in perovskite solar cells. MoS\(_2\)/TiO\(_2\) composite enhanced the absorption range of solar cells from 350 to 800 nm. Power conversion efficiency (PCE) obtained was increased from 3.74% to 4.43% as compared to pure TiO\(_2\) based perovskite solar cells.

4.5. MoS\(_2\) in Silicon-Based Heterojunction Solar Cells

2D materials exhibit distinctive optoelectronic features that are appropriate for manufacturing 2D-materials based solar cells. Among TMDCs, MoS\(_2\) shows fascinating optoelectronic attributes and its band gap influenced by the number of layers [247–249]. Abundant research has been accompanied related to optoelectronic characteristics, conversion of solar energy, light emission, and heterostructures of TMDCs [250–252].

Shanmugam et al. [231] manufactured Schottky-barrier solar cells. Nanomembranes of MoS\(_2\) were used as a photoactive layer and PCE of 0.7% was achieved for MoS\(_2\) with 110 nm thickness using ITO/MoS\(_2\)/Au based solar cell. For 220 nm thick MoS\(_2\) based solar cells, PCE of 1.8% was achieved. A similar group reported PCE of 1.3% using ITO/TiO\(_2\)/MoS\(_2\)/P3HT/Au based bulk heterojunction solar cells. Tsai et al. [231] utilized monolayer of n-MoS\(_2\) with the p-silicon substrate to fabricate heterojunction based solar cells. Al/MoS\(_2\)/p-Si/Cr-Ag based heterojunction solar cell gave J\(_{SC}\) of 22.36 mA/cm\(^2\), PCE of 5.23%, fill factor (FF) of 57.26% and VOC of 0.41 V in contrast to J\(_{SC}\) of 21.66 mA/cm\(^2\), FF of 56.02% and VOC of 0.38 V for Al/p-Si based solar cells. Figure 4c is the simplified sketching of Al/MoS\(_2\)/p-Si/Cr-Ag based heterojunction solar cell [231]. Hao et al. [253] fabricated p-n junction based MoS\(_2\)/Si solar cells. MoS\(_2\) transferred to the p-type silicon substrate by magnetron sputtering and gave VOC of 0.14 V, PCE of 1.3%, FF of 42.4%, and J\(_{SC}\) of 3.2 mA/cm\(^2\). To overcome the transfer process of the as-synthesized MoS\(_2\) layer on the substrate, Hasani et al. [254] synthesized MoS\(_2\) directly on substrate in n-MoS\(_2\)/p-Si-based heterostructure device.

Jiao et al. [255] studied the effect of MoS\(_2\) in graphene/silicon-based solar cells. MoS\(_2\) performed the function of the interfacial layer in this scenario and gave PCE of 4.4%. Jiao et al. [255] also studied the effect of annealing temperature on the MoS\(_2\) prototype which affects the PCE of the device. The same group reported PCE of 6.6% achieved by silicon substrate surface passivation. Hao et al. [256] deposited MoS\(_2\) on p-type silicon substrate buffered with SiO\(_2\). They studied photovoltaic features of Pd/MoS\(_2\)/(3–5 nm) SiO\(_2\)/Si based heterojunction solar cell with SiO\(_2\) buffer layer and without SiO\(_2\) buffer layer. MoS\(_2\)/Si based heterojunction solar cell gave PCE of 1.4% and after incorporation of SiO\(_2\) buffer layer PCE increased by three-fold (4.5%). Buffer layer reduces the chances of recombination of electrons and holes. PCE of 15.8% was achieved by using MoS\(_2\) in graphene/silicon solar cells [252]. Graphene/MoS\(_2\)/Si based heterojunction solar cell gave a better performance like J\(_{SC}\) of 26.6 mA/cm\(^2\), FF of 62% and VOC of 0.50 V as compared to the device without MoS\(_2\) with open-circuit voltage (VOC) of 0.45 V, fill factor (FF) of 54% and short-circuit current density (Jsc) of 25.6 mA/cm\(^2\).

Tsuboi et al. [257] used MoS\(_2\) between graphene and silicon substrate as an electron blocking and passivation layer in graphene/MoS\(_2\)/n-Si-based heterojunction solar cells. Higher PCE of 1.35% was achieved with MoS\(_2\) as compared to PCE of 0.07% without the incorporation of MoS\(_2\) in the device. PCE increased to 8.0% by using tri-layer graphene in the solar cell. Power conversion efficiency (PCE) increased by increasing the number of layers of graphene. MoS\(_2\) with a thickness of 9 nm in tri-layer graphene/MoS\(_2\)/n-Si-based heterojunction solar cells gave PCE of 11.1%. Van der Waals
based MoS$_2$/WSe$_2$ heterostructures being fabricated by Furchi et al. [258] on SiO$_2$/silicon substrate. Graphene/MoS$_2$ and WS$_2$/MoS$_2$ heterostructures have gained research interest as they carry a powerful role in electronic appliances [259–263]. Al$_2$O$_3$ used as passivation layer in MoS$_2$/silicon-based heterojunction solar cell [264]. Power conversion efficiency (PCE) of 5.6% can be obtained by passivating MoS$_2$ surface by Al$_2$O$_3$ as compared to PCE of 2.21% achieved by MoS$_2$/silicon-based device without Al$_2$O$_3$ passivation layer.

MoS$_2$/silicon heterojunction solar cell was fabricated by the direct buildup of MoS$_2$ on the substrate by the sol-gel method [265]. ITO/MoS$_2$/p-Si/Ag-based solar cell showed enhanced photovoltaic performance. By in situ growth of MoS$_2$, defects at the interface were reduced, higher VOC accredited to the emergence of heterojunction at MoS$_2$/silicon interface and due to reduction in defects at interface, recombination losses also decreased, consequently Jsc increased. Mueller and coworkers [258] fabricated WSe$_2$/MoS$_2$ based heterostructure and achieved a power conversion efficiency of 0.2%. In bulk heterojunction solar cells, the major restriction is limited absorption range (≈100–200 nm) of polymers as compared to silicon. To get better absorption and performance of solar cells, tandem solar cells evolved. Several single-junction based solar cells piled up vertically in tandem solar cell design [266]. This stacking reduces the thermalization effect because each part of the vertical stack absorbs a specific part of sunlight. Saraswat et al. [267] manufactured most effective TMDCs/silicon-based tandem solar cells.

5. Summary and Outlook

Here, in this review, we have summed up the subclasses of 2Ds with their respective crystalline structures, synthetic strategies, optoelectric properties, and applications of TMDCs particularly MoS$_2$ in solar cell devices. Functioning of MoS$_2$, specifically in DSSCs, Organic solar cells, perovskite solar cells, and in silicon heterojunction solar cells has been briefly analyzed in this review. 2D materials, especially TMDCs having fascinating properties, come up with great research interest to cater the innovative opportunities among research groups to investigate the concepts and phenomena in energy, electronics, and optoelectronics. Taking into consideration, authentic fabrication methods have developed for 2D materials including micromechanical cleavage strategy, which offers high-quality nanosheets, but this method is known with lab-scale production and cannot cope with industrial needs. Along with micromechanical cleavage, liquid-based exfoliation, electrochemical exfoliation, and CVD also give reliable results for different applications. Graphene-affiliated research has been reached in maturity after an in-depth investigation of many years. Now, layered TMDCs provoking new thrill in research because of their captivating properties such as cost-effective, tunable work function, catalytic effect, high absorption coefficient, strong light-matter interaction, and thickness-dependent bandgap. Due to the atomically thin layered structure, enhanced optical and electric properties, TMDCs have a wide range of applications in photovoltaic devices. MoS$_2$, in DSSCs, can be used as a counter electrode replacing conventional expensive and less stable platinum counter electrode and gives enhanced power conversion efficiency of 7.50% as compared to the platinum electrode. To fulfill increasing energy demands, third-generation solar cells, organic and perovskite, play a vital role. Due to the tunability of work function, MoS$_2$ can be used as both an electron extractor and a hole extractor layer in organic and perovskite solar cells. MoS$_2$ can be used as a buffer layer, interfacial layer, electron transport layer, and as a hole transport layer in organic solar cells. Power conversion efficiency (PCE) of 8.43% achieved by using MoS$_2$ in organic solar cells. MoS$_2$ in perovskite solar cells exhibited a power conversion efficiency of 9.53%, higher than the device containing PEDOT: PSS as the hole transport layer. In another scenario of perovskites, TiO$_2$/CH$_3$NH$_3$PbI$_3$/MoS$_2$/Spiro-OMeTAD/Au, PCE of 13.3% was achieved. Perovskite solar cells incorporating MoS$_2$ gave PCE of 20.4%. In the present literature survey, heterojunction solar cells are also analyzed. 2D (two-dimensional) /2D van der Waals heterostructures enhance watt per gram usage of photo-active material. Graphene/MoS$_2$, WS$_2$/MoS$_2$, and MoS$_2$/Si based heterojunction solar cells with varying values of power conversion efficiencies have also been summarized there. A large number of research groups are working on the emerging
field of TMDCs, but still, in many ways, this field is in premature stage with various transition metal dichalcogenides which are not investigated and fabricated yet and which could be the source of the novel as well as enchanting discoveries. More research should pay attention to incorporating TMDCs in various types of solar cells to enhance the PCE.

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