

# An comprehensive review of Molybdenum nanomaterials

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In the past few decades, there have been significant developments in nanotechnology in various areas. The present work focuses on the Molybdenum-based nanomaterials which have shown promising applications in the field of electronic and energy storage devices. Molybdenum nanomaterials have characteristics next to graphene nanomaterials. Nano-scale forms of molybdenum oxide and molybdenum sulfide are excellent materials for supercapacitor electrodes. The review indicates different methods preferred for the synthesis of molybdenum-based nanomaterials.

**Keywords:** Molybdenum nanomaterials, electronic, energy, molybdenum oxide, molybdenum sulfide, supercapacitor

## Introduction

The demand and the advance in the development of flexible, portable electronic and energy storage devices are based on the energy storage devices such as fuel cells and supercapacitors. Supercapacitors are electrochemical capacitors, which act as a linking bridge between batteries and conventional capacitors. Batteries have higher specific energy for lower specific power and capacitors usually have low specific energy over the high specific power, whereas, supercapacitor shows higher power densities, short charging time, and long discharging time compared to batteries and an excellent specific capacitance and high energy densities than the traditional capacitors [1].

Electrochemical double-layer Capacitors and Pseudocapacitors are the two types of supercapacitors. Electrochemical double-layer capacitors employ electrostatic adsorption at the electrode and electrolyte interface to store energy. These include nanoporous carbonaceous materials which are defined with high specific surface area, high conductivity, and high mechanical conductivity. Pseudocapacitors prefer transition metal oxides and conducting polymers, as quick and reversible redox reaction takes place nearby / on to the surface of the electrodes in the process of the storage of charge [2,3].

Higher capacitances and energy densities are exhibited by pseudocapacitors, cost-effective over the electrochemical double-layer capacitors. Examples of transition metal oxides electrodes for pseudocapacitors are ruthenium oxide, manganese dioxide, and cobalt oxide. Conducting polymers such as polyaniline, polypyrrole and polythiophene can be used as pseudo capacitor electrodes [4,5].

However, the growing demand for energy storage devices led to the development of new types of electrode materials. Therefore, the research of nanometer-scale metal oxide and sulfide as the material of supercapacitor electrodes has become a new field. For example, cobalt sulfide (CoS, CoS<sub>2</sub>), nickel sulfide (NiS, NiS<sub>2</sub>, Ni<sub>3</sub>S<sub>2</sub>), molybdenum sulfide (MoS<sub>2</sub>), copper sulfide (CuS, Cu<sub>2</sub>S), and vanadium sulfide (VS, VS<sub>2</sub>) have been used as supercapacitors electrode materials [6 - 8].

Transition metal dichalcogenides (TMDs) are of great potential for the use of next-generation electronic devices. Of these, semiconducting TMDs can be produced by combining the metals (M)W and Mo with ore-forming chalcogens (X) S or Se in the form MX<sub>2</sub>. These materials have a structure that consists of strong in-plane covalent bonds (X–M–X) that create isolated atomic layers resulting in a bulk crystal when they interact with one another through weak van der Waals forces [9-11].

Electronic properties of the material change with the number of layers. Monolayer exhibits a direct bandgap, when the layer increases, materials show an indirect bandgap with its bulk structure. this fact is identified by spectroscopic and electronic studies in the mechanically exfoliated MoS<sub>2</sub> and other semiconducting TMDs [12, 13]. Mineral crystals are used for the isolation of monolayers of MoS<sub>2</sub> by exfoliation through different top-down approaches, including mechanical exfoliation [10,14], chemical exfoliation [15], and ultrasonic treatments [16].

In recent years, the contribution of Molybdenum oxide (MoO<sub>3</sub>) and molybdenum sulfide (MoS<sub>2</sub>) related materials has been identified [6]. As it stimulated interest among other transition metal sulfides due to its layered structure and inherent conductivity,[17] and it is considered to be a suitable replacement for graphene and carbon nanotubes in energy storage applications. In addition, molybdenum-based materials (such as MoO<sub>3</sub>, MoO<sub>2</sub>, and MoS<sub>2</sub>) exhibit various valences and rich chemical properties, making them viable candidate materials for electrochemical applications [18].

## Synthesis of Molybdenum sulfide nanoparticles

MoS<sub>2</sub> is a transition metal sulfide with a layered structure, where a metal molybdenum layer is sandwiched between two sulfur layers with weak van der Waals forces, and the interlayer S–Mo–S atoms are strongly linked with covalently [19-21]. MoS<sub>2</sub> possesses unique physicochemical properties due to its unique atomic and electronic structure. It has application in solid lubricants, catalysts, supercapacitors, and lithium-ion batteries [22-24]. Among these, the research on the application of MoS<sub>2</sub> as a supercapacitor electrode material is the most extensive.

Soon *et al.* found that the MoS<sub>2</sub> nano-film presented an electric double layer capacitance behaviour [25].

Ma *et al.* reported that nano-MoS<sub>2</sub> intercalated in polypyrrole could improve its capacitance performance [26].

Cao *et al.* fabricated micro-supercapacitors using coated MoS<sub>2</sub> nanofilms and showed that MoS<sub>2</sub> has excellent electrochemical performance in aqueous electrolytes due to its structure. Usually, two-dimensional electrochemical electrodes face inadequate contact with the electrolyte and hence low surface area utilization efficiency. Numerous efforts have been made to design three-dimensional (3D) electrodes, such as MoS<sub>2</sub>/mesoporous carbon spheres. Recently, there have been some reports related to NiCo<sub>2</sub>S<sub>4</sub> and graphene oxide composites applied in supercapacitors [27].

Krishnamoorthy *et al.* reported specific capacitance of chemically prepared MoS<sub>2</sub> nanostructure as 92.85 F/g [28].

Huang *et al.* reported polyaniline/MoS<sub>2</sub> composites as supercapacitor electrodes with the specific capacitance of 575 F/g. With the hydrothermal method, flower-like molybdenum disulfide microspheres were synthesized. It can be used as a supercapacitor electrode and exhibited high specific capacitance (518.7 F/g) and excellent cycling performance (88.2% retention after the completion of 2500 cycles). In addition, a high-performance symmetric supercapacitor was successfully fabricated by using MoS<sub>2</sub> as both positive electrode and negative electrode, which exhibited a high energy density of 12.46 W h/kg at a power density of 70 W/kg [29].

Molybdenum disulfide (MoS<sub>2</sub>) is a material having fascinating properties, like high surface area, higher ionic conductivity than metal oxides [30], and good mechanical flexibility [31]. Hence, its application is extended towards in the field of electronic appliances, gas sensors, supercapacitors, batteries, hydrogen evolution reactions [28, 32-35]. The MoS<sub>2</sub> nanosheets are synthesized either by bottom-up approaches, such as hydrothermal, chemical vapor deposition (CVD), or by top-down approaches, like, ball milling, mechanical exfoliation, and liquid phase exfoliation [28, 36-39].

Among them, liquid-phase exfoliation is the simple and high-yielding route to prepare the MoS<sub>2</sub> nanosheets. The solvents such as ethanol, dimethylformamide (DMF), N-Methyl-2-pyrrolidone (NMP) are used to exfoliate the bulk MoS<sub>2</sub> particles into nanosheets [39,40]. The MoS<sub>2</sub> nanosheets are proved to improve the electrochemical performance of materials like Co<sub>3</sub>O<sub>4</sub>, polyethylene dioxythiophene (PEDOT), polyaniline (PANI), and Mn<sub>3</sub>O<sub>4</sub> [29, 41-43]. The mixture of MoS<sub>2</sub> and n-butyllithium (2.5 M in hexanes) was autoclaved at 90°C for 12h with stirring, the product formed was filtered and washed with anhydrous hexane. It was vacuum dried and subjected to ultrasonication. The obtained suspension was then neutralized with 1 M HCl and the product obtained was washed with distilled water-methanol, finally, it is subjected to freeze-drying [44].

Three-dimensional flower-like molybdenum disulfide microspheres composed of nanosheets were prepared by a hydrothermal method using ammonium molybdate as the molybdenum source and thiourea as the sulfur source. Structural and morphological characterizations were performed by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive X-ray (EDX) spectroscopy, and X-ray photoelectron spectroscopy (XPS).

The electrochemical properties of MoS<sub>2</sub> electrode were studied by performing cyclic voltammetry (CV), galvanostatic charge-discharge analysis, and electrochemical impedance spectroscopy (EIS). When used as an electrode material for supercapacitor, the hybrid MoS<sub>2</sub> showed a high specific capacity of 518.7 F/g at a current density of 1 A/g and 275 F/g at a high discharge current density of 10 A/g. In addition, a proportional supercapacitor composed of MoS<sub>2</sub> showed high energy density. The outstanding performance of the MoS<sub>2</sub> electrode material indicates its great potential for applications in the high-performance energy storage system [45].

Molybdenum Oxide (MoO<sub>3</sub>) is a prominent transition metal oxide with rich polymorphism and structural litheness [7], with many valences and unique structure with outstanding specific capacitance [46]. The electrochromic and catalytic properties are important in storage media, gas sensors, and organic solar cells. It possesses greater electrochromic and catalytic properties [17] that can potentially be functional in storage media [47], gas sensors [48] and humidity sensors [49], organic solar cells [50]. The oxidation states of molybdenum oxide range from + 2 to + 6 and predominantly exist in two primary forms, viz., molybdenum (IV) oxide and molybdenum (VI) oxide [51]. Solution combustion [52, 53], sol-gel [54], microwave [55], and green synthesis methods [56] are the common techniques preferred for the synthesis of molybdenum oxide nanoparticles. Of which, the hydrothermal procedure [57] is preferred for the preparation of molybdenum oxide nanoparticles. Molybdenum oxide nanoparticles are obtained in different morphologies such as nanobelts [58], nanoflowers [59], nanowires [60], and nanocubes [61] can be obtained. These morphologies are important in knowing the specific capacitance of the substantial. With the hydrothermal method, the effect of parameters such as temperature, pressure, and reaction time on the physiochemical performance of the material can be determined [62].

### Synthesis of Molybdenum oxide nanoparticles

Miao *et al.* reported the synthesis of Molybdenum Trioxide nanostructures by cost-effective metal-assisted chemical wet etching method, with this method material indicated a specific capacitance of 30.85 F/g in 0.5M Na<sub>2</sub>SO<sub>4</sub> electrolyte solution [63].

Wang *et al.* synthesized α-MoO<sub>3</sub> nanorods through the hydrothermal method and observed that annealed α-MoO<sub>3</sub> nanorods demonstrated excellent specific capacitance compared to hydrothermally obtain ones [64].

Shakir *et al.* reported the preparation of orthorhombic molybdenum trioxide nanowires using a hydrothermal method which yielded a specific capacitance of 168 F/g at 0.5/Ag current density and 97% cyclic retention in 1M H<sub>2</sub>SO<sub>4</sub> electrolyte solution [65].

In the above-reported works, very high concentrations of electrolyte were used for determining the electrochemical performance of the synthesized molybdenum oxide nanomaterials. In the synthesis of molybdenum oxide nanorods hydrothermal method is preferred, and its electrochemical studies were based on the low concentration of electrolyte, carrying exceptional rate competence and high specific capacitance.

Ultrasonication-assisted liquid-phase exfoliation method was considered for the preparation of MoS<sub>2</sub> nanosheets [66]. Polyvinylpyrrolidone (PVP, MW ~ 40,000) was dissolved in ethanol to bulk MoS<sub>2</sub> powder. The mixture was ultrasonicated to exfoliate MoS<sub>2</sub> nanosheets. The exfoliated MoS<sub>2</sub> sheets which remained on top of the solution were subjected to post-treatment with isopropyl alcohol (IPA).

The hydrothermal method was followed for the synthesis of Molybdenum oxide nanostructures. Ammonium Heptamolybdate Tetrahydrate solution was treated with 0.01M sodium dodecyl sulfate on stirring and pH was maintained to 3 with the dilute HCl. Hydrothermal treatment was given in the Teflon-lined stainless-steel autoclave 180°C for 24 h. the precipitate formed was washed with water and ethanol and the precipitate was obtained on centrifugation was subjected to drying at 60 °C overnight to get dry powder [1].

With modified alumina powder in the solution of molybdenum(V) chloride in ethanol, Alumina/molybdenum nanocomposites were obtained. Modified alumina powder was subjected to calcined at low temperature to eliminate the organic residue. It was followed with reduction steps to form obtain 2–10 nm metallic nanoparticles on the surface of the alumina crystals. The method indicated the formation of microstructure with improved mechanical behaviour [67].

So, it is presumed that the electrochemical stability of the SnO<sub>2</sub> could be improved by using MoS<sub>2</sub> nanosheets along with the SnO<sub>2</sub> nanoparticles. There are very limited studies reported focussing on the supercapacitor application with the combination of MoS<sub>2</sub>–SnO<sub>2</sub> phases as nanocomposite [68]. The hydrothermal method is the widely used technique to prepare MoS<sub>2</sub>–SnO<sub>2</sub> nanocomposite with the ligand exchange process [69], SnO<sub>2</sub> nanoparticles are functionalized onto the surface of the MoS<sub>2</sub> nanosheets at room temperature. The route is expected to be energy-saving and produce the MoS<sub>2</sub>–SnO<sub>2</sub> nanocomposite which will serve as a good supercapacitor electrode material.

According to Ziying *et al.*, MoS<sub>2</sub>-RGO hybrids were prepared by self-assembly of MoS<sub>2</sub> NPs and GO nanosheets, followed by hydrothermal treatment [70].

In the study conducted by Yun *et al.*, for the synthesis of MoS<sub>2</sub>/GO nanocomposites, the bulk MoS<sub>2</sub>, was mixed with stock solutions of GO by sonication for 40 h, respectively. As a control, bulk MoS<sub>2</sub> was sonicated alone in deionized water. The mixture was subjected to settling and then centrifuged to obtain the final precipitate [71].

As per Bin *et al.*, a mixture of MoS<sub>2</sub> or M-MoS<sub>2</sub> in acetone was subjected to magnetic stirring at room temperature followed by sonication with the addition of epoxy resin. The contents will be subjected to vacuum distillation under stirring with a magnetic stirrer at 80 °C. On cooling a stoichiometric amount of curing agent (D<sub>230</sub>) corresponding to 100% of EP resin content was added and stirred for some time. The resulting mixture was cured and post-cured to obtain the final nanocomposite [72].

Amine-functionalized MoS<sub>2</sub> and acyl chloride-coordinated ND, chemically conjugated nanodiamond (ND)/MoS<sub>2</sub> nanocomposite was formed and its structure with morphology were analyzed to know the scattering of MoS<sub>2</sub> on the ND platform. The study revealed that the efficient electron capacity of the ND/MoS<sub>2</sub> nanocomposite was considerably greater than that of the MoS<sub>2</sub> electrode alone. Therefore, the nanophase electrode showed higher electrochemical capacitance than that of the MoS<sub>2</sub> electrode alone [73].

## Characterization

Powder X-ray diffraction (XRD) data were recorded on a diffractometer with Cu K $\alpha$  radiation Transmission electron microscope [74].

The morphology of the as-synthesized molybdenum oxide nanorods was determined by Field Emission Scanning Electron Microscopy.

Powder X-ray diffraction (XRD) data patterns were recorded on a diffractometer with Cu K $\alpha$  radiation Transmission electron microscope

The maximum absorbance of Molybdenum nanomaterials was determined using UV–visible spectroscopy employing UV/Vis spectrophotometer.

FTIR spectra of the samples were obtained at ambient temperature using the KBr disk method employing an FTIR spectrophotometer.

The electrochemical measurement of as-synthesized MoO<sub>3</sub> nanorods was analyzed by cyclic voltammetry, galvanometric charge-discharge, and electrochemical impedance spectroscopy [1].

## Conclusion

The review highlighted about the synthesis of molybdenum nanomaterials by different approaches, of which it is clear that the hydrothermal method is preferred for the synthesis of molybdenum-based nanomaterials.

Also, the review indicated that the structural and morphological characterization study was done with XRD, SEM, TEM, EDX and XPS. Further study revealed that molybdenum-based nanomaterials have excellent electrochemical properties as it showed high energy density due to which can be considered in the application of high-performance energy storage systems.

## Conflicts of interest

There are no conflicts to declare

## References

- [1] R. Kiran Kumar Reddy, Saraswathi Kailasa, B. Geetha Rani, N. Jayarambabu, Hayashi Yasuhiko, G. Venkata Ramana and Venkateswara Rao, “ Hydrothermal approached 1-D

- molybdenum oxide nanostructures for high-performance supercapacitor application”, *SN Applied Sciences.*, vol. 1, (2019), pp. 1365
- [2] M. Zhi, C. Xiang, J. Li, M. Li and N. Wu, “Nanostructured carbon-metal oxide composite electrodes for supercapacitors: a review”, *Nanoscale.*, vol.5, (2013), pp.72–88.
- [3] A. W. Anwar, A. Majeed, N. Iqbal, W. Ullah, A. Shuaib, U. Ilyas and H.M. Rafque, “Specific capacitance and cyclic stability of graphene-based metal/metal oxide nanocomposites: a review”, *J Mater Sci Technol.*, vol. 31, (2015), pp. 699–707.
- [4] W. Deng, X. Ji, Q. Chen and C.E. Banks, “Electrochemical capacitors utilizing transition metal oxides: an update of recent developments”, *RSC Adv.*, vol.1, (2011), pp.1171–1178.
- [5] M. Moussa, M.F. El-Kady, Z. Zhao, P. Majewski, J. Ma, “Recent progress and performance evaluation for polyaniline/graphene nanocomposites as supercapacitor electrodes”, *Nanotechnology.*, vol.27, no. 44, (2016), pp. 442001.
- [6] A. Chithambararaj and A.C. Bose, “Investigation on structural, thermal, optical, and sensing properties of meta-stable hexagonal MoO<sub>3</sub> nanocrystals of one-dimensional structure”, *Beilstein J Nanotechnol.*, vol. 2, (2011), pp. 585.
- [7] N. Maheswari, G. Muralidharan, “Controlled synthesis of nanostructured molybdenum oxide electrodes for high-performance supercapacitor devices”, *Appl Surf Sci.*, vol. 416, (2017), pp. 461–469.
- [8] W. J. Zhang and K. J. Huang, “A review of recent progress in molybdenum disulfide-based supercapacitors and batteries”, *Inorg. Chem. Front.*, vol. 4, no.10, (2017), pp.1602–1620.
- [9] P. Joensen, R.F. Frindt and S.R. Morrison, “Single-layer MoS<sub>2</sub>”, *1986 Mater. Res. Bull.*, vol. 21, (1986), pp. 457–61.
- [10] K.S. Novoselov, D. Jiang, F. Schedin, T.J. Booth, V.V. Khotkevich, S.V. Morozov and A. K. Geim, “Two-dimensional atomic crystals”, vol. 102, *Proc. Natl. Acad. Sci. USA*, (2005), pp. 10451–10453.
- [11] R.F. Frindt and A.D. Yoffe, “Physical Properties of Layer Structures: Optical Properties and Photoconductivity of Thin Crystals of Molybdenum Disulphide”, vol. 273, *Proc. R. Soc. Lond. Ser. A.*, (1963), pp. 69–83.
- [12] A. Splendiani, L. Sun, Y.B. Zhang, T.S. Li, J. Kim, C.Y. Chim, G. Galli and F. Wang, “Emerging Photoluminescence in Monolayer MoS<sub>2</sub>”, vol. 10, *Nano Lett.*, vol.10, (2010), pp. 1271–1275.
- [13] K.F. Mak, C. Lee, J. Hone, J. Shan and T.F. Heinz T F, “Atomically thin MoS<sub>2</sub>: a new direct-gap semiconductor”, vol. 105, no.13, *Phys. Rev. Lett.*, (2010), pp.136805
- [14] B. Radisavljevic, A. Radenovic, J.Brivio, V.Giacometti and A.Kis, “ Single-layer MoS<sub>2</sub> transistors”, vol.6, *Nat. Nanotechnol.* (2011), pp.147–50.
- [15] G. Eda, H. Yamaguchi, D. Voiry, T. Fujita, M. Chen and M. Chhowalla, “Photoluminescence from Chemically Exfoliated MoS<sub>2</sub> ”, vol. 11, no.12, *Nano Lett.*, (2011), 5111–5116.
- [16] V. Stengl V and J. Henych, “Strongly luminescent monolayered MoS<sub>2</sub> prepared by effective ultrasound exfoliation”, vol.5, *Nanoscale*, (2013), 3387–94.
- [17] T. H. Chiang, P.Y. Ho, S.Y. Chiu and A.C. Chao, “Synthesis, characterization and photocatalytic activity of  $\alpha$ -MoO<sub>3</sub> particles utilizing different polyol monomers under visible light irradiation”, vol.651, *J Alloy Compd.*, (2015), 106–113
- [18] F. Wang, G. Li, J. Zheng, J.Ma, C.Yang and Q. Wang, “Hydrothermal synthesis of flower-like molybdenum disulfide microspheres and their application in electrochemical supercapacitors”, vol.8, *RSC Adv.*, (2018), 38945–38954
- [19] L. Wang, Z. Xu, W. Wang, and X. Bai, “Atomic mechanism of dynamic electrochemical lithiation processes of MoS<sub>2</sub> nanosheets”, vol.136, *J. Am. Chem. Soc.*, (2014), pp.6693–6697.
- [20] X. Zhao, J. Sui, F. Li, H. Fang, H. Wang, J. Li, W. Cai and G. Cao, “Lamellar MoSe<sub>2</sub> nanosheets embedded with MoO<sub>2</sub> nanoparticles: novel hybrid nanostructures promoted excellent performances for lithium-ion batteries”, vol. 8, *Nanoscale*, (2016), pp. 17902–17910.
- [21] Y. Shi, W. Zhou, A. Y. Lu, W. Fang, Y. H. Lee, A. L. Hsu, S. M. Kim, K. K. Kim, H. Y. Yang, L. J. Li, J. C. Idrobo and J. K. van der, “Waal epitaxy of MoS<sub>2</sub> layers using graphene as growth templates”, vol.12, *Nano Lett.*, (2012), pp. 2784–2791.
- [22] Y. H. Lee, X. Q. Zhang, W. Zhang, M. T. Chang, C. T. Lin, K. D. Chang, Y. C. Yu, J. W. Wang, C. S. Chang, L. J. Li and T. W. Lin, “Synthesis of large-area MoS<sub>2</sub> atomic layers with chemical vapor deposition”, vol.24, *Adv. Mater.*, (2012), pp. 2320–2325.
- [23] M. Acerce, D. Voiry and M. Chhowalla, “Metallic 1T phase MoS<sub>2</sub> nanosheets as supercapacitor electrode materials”, vol. 10, *Nat. Nanotechnol.*, (2015), pp. 313–318.

- [24] K. Bindumadhavan, S. K. Srivastava and S. Mahanty, "MoS<sub>2</sub>- MWCNT hybrids as a superior anode in lithium-ion batteries", vol. 49, Chem. Commun., (2013), pp. 1823–1825.
- [25] J. M. Soon and K. P. Loh, "Electrochemical double-layer capacitance of MoS<sub>2</sub> nanowall films", vol.10, Electrochem. SolidState Lett., (2007), pp. 250–254.
- [26] G. Ma, H. Peng, J. Mu, H. Huang, X. Zhou, and Z. Lei, "In situ intercalative polymerization of pyrrole in graphene analogue of MoS<sub>2</sub> as advanced electrode material in a supercapacitor", vol.229, J. Power Sources., (2013), pp.72–78.
- [27] L. Cao, S. Yang, W. Gao, Z. Liu, Y. Gong, L. Ma, G. Shi, S. Lei, Y. Zhang, S. Zhang, R. Vajtai and P. M. Ajayan, "Direct laser patterned micro-supercapacitors from paintable MoS<sub>2</sub> films", vol.9, Small., (2013), 2905–2910.
- [28] K. Krishnamoorthy, P. Pazhamalai, G.K. Veerasubramani and S.J. Kim, "Mechanically delaminated few-layered MoS<sub>2</sub> nanosheets based high-performance wire type solid-state symmetric supercapacitors", vol. 321, J. Power Sources., (2016), 112–119.
- [29] K. J. Huang, L. Wang, Y. J. Liu, H. B. Wang, Y. M. Liu, and L. L. Wang, "Synthesis of polyaniline/2-dimensional graphene analog MoS<sub>2</sub> composites for high-performance supercapacitor", vol.109, Electrochim. Acta., (2013), 587–594.
- [30] N. Zheng, X. Bu and P.Feng, " Synthetic design of crystalline inorganic chalcogenides exhibiting fast-ion conductivity, vol. 426, Nature., (2003), pp.428–32.
- [31] M. Chhowalla, H.S. Shin, G. Eda, L. J. Li, K.P. Loh and H. Zhang, "The chemistry of two-dimensional layered transition metal nanosheets", vol. 5, Nat. Chem., (2013), pp. 263–275.
- [32] S. Cui, Z. Wen, X. Huang, J. Chang and J. Chen, "Stabilizing MoS<sub>2</sub> nanosheets through SnO<sub>2</sub> nanocrystal decoration for high-performance gas sensing in air", vol.11, no.19, Small., (2015), pp. 2305–2313.
- [33] T. Yang, Y. Chen, B. Qu, L. Mei, D. Lei, H. Zhang, Q. Li and T. Wang, "Construction of 3D flower-like MoS<sub>2</sub> spheres with nanosheets as anode materials for high-performance lithium-ion batteries", vol.115, Electrochem. Acta., (2014), pp 165–169.
- [34] K. Chang, X. Hai, H. Pang, H. Zhang, L. Shi, G. Liu, H. Liu, G. Zhao, M. Li and J. Ye, "Targeted synthesis of 2H- and 1T-Phase MoS<sub>2</sub> monolayers for catalytic hydrogen evolution", vol. 28, Adv. Mater., (2016), pp. 10033–10041.
- [35] A.A. Bessonov, M.N. Kirikova, D.I. Petukhov, M. Allen, T. Ryhanen and M.J.A. Bailey, "Layered memristive and memcapacitive switches for printable electronics", vol.14, Nat. Mater., (2014), pp.199–204.
- [36] X. Ren, L. Pang, Y.Zhang, X.Ren, H.Fan and S. Liu (Frank), "One-step hydrothermal synthesis of monolayer MoS<sub>2</sub> quantum dots for highly efficient electrocatalytic hydrogen evolution", Vol. A3, J. Mater. Chem., (2015), pp. 10693–10697
- [37] Y. Yu, C. Li, Y. Liu, L. Su, Y. Zhang and L.Cao, 2013 "Controlled scalable synthesis of uniform, high-quality monolayer, and few-layer MoS<sub>2</sub> films", vol.3, Sci. Rep., (2013), pp. 1866.
- [38] J. Kwon, Y.K. Hong, H.J. Kwon, Y.J. Park, B. Yoo, J. Kim, C.P. Grigoropoulos, M.S. Oh and S. Kim, "Optically transparent thin-film transistors based on 2D multilayer MoS<sub>2</sub> and indium zinc oxide electrodes", vol.26, Nanotechnology., (2015), pp. 035202.
- [39] Q. Weng, X. Wang, C. Zhang, X. Jiang, Y. Bando and D. Golberg, 2015 "Supercapacitive energy storage performance of molybdenum disulfide nanosheets wrapped with microporous carbons", vol.3, J. Mater. Chem. A Mater. Energy Sustain., (2015), pp.3097–3102.
- [40] F. Ghasemi and S. Mohajerzadeh, S 2016 "Sequential solvent exchange method for controlled exfoliation of MoS<sub>2</sub> suitable for phototransistor fabrication", vol.8, ACS Appl. Mater. Interfaces, (2016), pp. 31179–31191.
- [41] D. Liang, Z. Tian, J. Liu, Y. Ye, S. Wu, Y. Cai and C. Liang, "MoS<sub>2</sub> nanosheets decorated with ultrafine Co<sub>3</sub>O<sub>4</sub> nanoparticles for high-performance electrochemical capacitors", Electrochim. Acta., (2015), pp. 376–382.
- [42] T. Alamro and M.K. Ram, "Polyethylenedioxythiophene and molybdenum disulfide nanocomposite electrodes for supercapacitor applications", vol. 235, Electrochim. Acta., (2017), pp. 623–631
- [43] M. Wang, H. Fei, P. Zhang and L. Yin, "Hierarchically layered MoS<sub>2</sub>/Mn<sub>3</sub>O<sub>4</sub> hybrid architectures for electrochemical supercapacitors with enhanced performance", vol. 209, Electrochim. Acta., (2016), pp. 389–398.
- [44] B. Chen, B. C. J. Ni, W. T. T. Liu, Q. Y. Ye, S.Y. Liu, H. X. Zhang and K. B. Yoon, "Mechanical properties of epoxy nanocomposites filled with melamine functionalized molybdenum disulfide", vol.8, RSC Adv., (2018), 20450.
- [45] F. Wang, G. Li, J. Zheng, J.Ma, C. Yang and Q. Wang, "Hydrothermal synthesis of flower-like molybdenum disulfide microspheres and their application in electrochemical supercapacitors", vol.8, RSC Adv., (2018), pp. 38945.
- [46] D. Wu, R. Shen, R. Yang, W. Ji, M. Jiang, W. Ding, L. Peng, "Mixed molybdenum oxides with superior performances as an advanced anode material for lithium-ion batteries", vol.7, Sci Rep., (2017), pp. 44697.

- [47] B. Yao, L. Huang, J. Zhang, X. Gao, J. Wu, Y. Cheng and J. Zhou, "Flexible transparent molybdenum trioxide nano paper for energy storage", vol.28, *Adv Mater.*, (2016), pp.6353–6358.
- [48] W.S. Kim, H.C. Kim and S.H. Hong, "Gas sensing properties of MoO<sub>3</sub> nanoparticles synthesized by solvothermal method", vol.12, *J. Nanoparticle Res.*, (2010), pp.1889–1896.
- [49] L. Khandare, S.S. Terdale and D.J. Late, "Ultra-fast  $\alpha$ -MoO<sub>3</sub> nanorod based humidity sensor", vol.2, *Adv Device Mater.*, (2016), pp.15–22.
- [50] K. Zilberberg, H. Gharbi, A. Behrendt, S. Trost and T. Riedl, "Low temperature, solution-processed MoO<sub>x</sub> for efficient and stable organic solar cells", vol.4, *ACS Appl Mater Interfaces*, (2012), pp.1164–1168
- [51] E. Zhou, C. Wang, Q. Zhao, Z. Li, M. Shao, X. Deng and X. Xu, "Facile synthesis of MoO<sub>2</sub> nanoparticles as high-performance supercapacitor electrodes and photocatalysts", vol.42, *Ceram Int.*, (2016), pp.2198–2203.
- [52] G.P. Nagabhushana, D.Samrat and G.T. Chandrappa, " $\alpha$ -MoO<sub>3</sub> nanoparticles: solution combustion synthesis, photocatalytic and electrochemical properties", vol.4, *RSC Adv.*, (2014), pp.56784–56790.
- [53] D. Parviz, M. Kazemini, A.M. Rashidi and K.J. Jozani, "Synthesis and characterization of MoO<sub>3</sub> nanostructures by solution combustion method employing morphology and size control", vol.12, *J. Nanoparticle Res.*, (2010), pp. 1509–1521.
- [54] W. Dong and B.Dunn, "Sol-gel synthesis and characterization of molybdenum oxide gels", vol.225, *J. Noncryst Solids.*, (1998), pp.135–140.
- [55] M. Manteghain, F. Tari and B. Bozorgi, "Microwave-assisted synthesis of molybdenum oxide nanoparticles", vol.1, *J Particle Sci Technol.*, (2015), pp.121–127
- [56] L. Fang, Y. Shu, A. Wang and T. Zhang, "Green synthesis and characterization of anisotropic uniform single-crystal  $\alpha$ -MoO<sub>3</sub> nanostructures", vol.111, *J Phys Chem C.*, (2007), pp.2401–2408.
- [57] U.K. Sen, S. Mitra, "Synthesis of molybdenum oxides and their electrochemical properties against Li", vol.54, *Energy Proc.*, (2014), pp.740–747.
- [58] S. Wang, Y. Zhang, X. Ma, W. Wang, X. Li, Z. Zhang, Y. Qian (2005) "Hydrothermal route to single-crystalline  $\alpha$ -MoO<sub>3</sub> nanobelts and hierarchical structures", vol.136, *Solid State Commun.*, (2005), pp. 283–287.
- [59] G. Li, L. Jiang, S. Pang, H. Peng and Z. Zhang, "Molybdenum trioxide nanostructures: the evolution from helical nanosheets to cross like nanoflowers to nanobelts", vol.110, *J Phys Chem.*, (2006), pp.24472–24475.
- [60] L. Mai, F. Yang, Y. X. Zhao, L. Xu, B. Hu and H. Liu, "Molybdenum oxide nanowires: synthesis & properties", vol.14, *Mater Today.*, (2011), pp.346–353.
- [61] S. Muthamizh, R. Suresh, K. Giribabu, R. Manigandan, S.P. Kumar, S. Munusamy, V. Narayanan, "Molybdenum oxide nanocubes: synthesis and characterizations", *AIP Conf Proc.*, (2015), pp. 1665:050155.
- [62] S. Bai, S. Chen, Y. Tian, R.Luo, D. Li and A. Chen, "Hydrothermal synthesis of  $\alpha$ -MoO<sub>3</sub> nanorods for NO<sub>2</sub> detection", vol.11, *Int J Nanosci.*, (2012), 1240044.
- [63] F. Miao, W. Wu, Q. Li, R. Miao and B. Tao, "Fabrication and application of molybdenum trioxide nanostructured materials for electrochemical capacitors", vol.12, *Int J Electrochem Sci.*, (2017), pp.12060–12073.
- [64] Y. Wang, Y. Zhu, Z. Xing and Y. Qian, "Hydrothermal synthesis of  $\alpha$ -MoO<sub>3</sub> and the influence of later heat treatment on its electrochemical properties. vol.8, *Int. J. Electrochem Sci.*, (2013), pp.9851–9857.
- [65] I. Shakir, M. Shahid, U. A. Rana, M.F. Warsi, "In situ hydrogenation of molybdenum oxide nanowires for enhanced supercapacitors", vol.4, *RSC Adv.*, (2014), pp.8741–8745.
- [66] J. Liu, Z. Zeng, X. Cao, G. Lu, L.H. Wang, Q.L. Fan, W. Huang and H. Zhang, 2012 "Preparation of MoS<sub>2</sub>-polyvinylpyrrolidone nanocomposites for flexible non-volatile rewritable memory devices with reduced graphene oxide electrodes", vol.8, *Small.*, (2012), pp.3517–3522.
- [67] L. A. Diaz, A. F. Valdes, C. A. Diaz . M. Espino R. Torrecillas, "Synthesis of molybdenum nanocomposites: Alumina/molybdenum nanocomposites obtained in organic media", vol. 23, no. 15, *Journal of the European Ceramic Society*, (2003), pp. 2829-2834.
- [68] L. Ma, X. Zhou, L. Xu, X. Xu and L. Zhang, "Microwave-assisted hydrothermal preparation of SnO<sub>2</sub>/MoS<sub>2</sub> composites and their electrochemical performance, vol. 11, no.2, *Nano.*, (2016), pp.16– 18.
- [69] Y. Chen, J. Lu, S. Wen, L. Lu and J. Xue, "Synthesis of SnO<sub>2</sub>/MoS<sub>2</sub> composites with different component ratios and their applications as lithium-ion battery anodes", vol.A2, *J. Mater. Chem.*, (2014), pp.17857–17866.
- [70] Z. Wang, T. Zhang, C. Zhao, T. Han, T.Fei, S.Liu and G.Lu, "Rational synthesis of molybdenum disulfide nanoparticles decorated reduced graphene oxide hybrids and their

application for high-performance NO<sub>2</sub> sensing”, vol.260, Sensors and Actuators B., (2018), pp. 1-43.

[71] Y. Liu, J. Peng, S. Wang, M. Xu, M.Gao, T. Xia, J. Weng, A. Xu and S. Liu, “Molybdenum disulfide/graphene oxide nanocomposites show favorable lung targeting and enhanced drug loading/tumor-killing efficacy with improved biocompatibility”, vol.10, NPG Asia Materials., (2018), e458.

[72] B. Chen, B. J. Ni, W. T. Liu, Q. Y. Ye, S. Y. Liu, H. X. Zhang and K. B. Yoon, “Mechanical properties of epoxy nanocomposites filled with melamine functionalized molybdenum disulfide”, vol.8, RSC Adv., (2018), pp.20450.

[73] Y.Kim, D. Lee, S. Y. Kim, E. Kang and C. K.Kim, “Nanocomposite Synthesis of Nanodiamond and Molybdenum Disulfide”, vol.9, Nanomaterials., (2019), pp.927.

[74] Z. Wang, T. Zhang, C. Zhao, T. Han, T. Fei, S. Liu and G. Lu, “Rational synthesis of molybdenum disulfide nanoparticles decorated reduced graphene oxide hybrids and their application for high-performance NO<sub>2</sub> sensing”, vol.260, Sensors and Actuators B., (2018), pp. 1-43