Transition Metal Dichalcogenides

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In recent years, the material characteristics and properties of transition metal dichalcogenide (TMDCs) have gained research interest in various fields, such as electronics, catalytic, energy storage. In particular, many researchers have been focusing on the applications of TMDCs in dealing with environmental pollution. TMDCs provide a unique opportunity to develop higher-value applications related to environmental matters. This work highlights the applications of TMDCs contributing to pollution reduction in (i) gas sensing technology, (ii) gas adsorption and removal, (iii) wastewater treatment, (iv) fuel cleaning, and (v) carbon dioxide valorisation and conversion. Overall, the applications of TMDCs have successfully demonstrated the advantages of contributing to environmental conversation due to their special properties. The challenges and bottlenecks of implementing TMDCs in the actual industry are also highlighted. More efforts need to be devoted to overcoming the hurdles to maximize the potential of TMDCs implementation in the industry.

Keywords: Transition Metal Dichalcogenide (TMDCs) ; Layered Materials ; Gas Cleaning ; Catalysis ; Pollution Reduction ; Emission Control

1. Introduction

Transition metal dichalcogenides (TMDCs) are a large family of two-dimensional (2D) layered materials, which are scientifically interesting and industrially important. These materials have attracted tremendous attention because of the unique structural features and interesting properties, such as optoelectronics, electronics, mechanical, optical, catalytical, energy-storage, thermal, and superconductivity properties [1][2][3][4][5][6][7]. TMDCs are the compounds of the chemical formula MX_2, where M is a transition metal element of groups IV-VII B.(Mo, W, V, Nb, Ta, Ti, Zr, Hf, Tc, Re) and X is a chalcogen element(S, Se, Te). The X-M-X unit layer consists of three atomic layers, in which one centre atom layer (M) is sandwiched between two chalcogen atom layers(X). TMDCs occupy the layered structures, which resemble that of graphite. The interlayers are stacked by weak van der Waals force, leading to the formation of monolayers or nanolayers from the bulk materials via exfoliation[8]. Different stacking of the layers along c-axis determines polymorphic crystal structures in TMDCs, and the common phases are 1T, 2H, 3R, and Td phases(T -trigonal, H -hexagonal, and R -rhombohedral, Td - distorted octahedral)[9].

2. Transition Metal Dichalcogenides in Pollution Reduction

There are more than 40 different TMDC types, including metals (such as TiS_2, VSe_2), superconductors (such as TaS_2, NbS_2), semimetals (such as $MoTe_2$, WTe_2), and semiconductors (MoS_2, $MoSe_2$, WS_2, WSe_2). TMDCs exhibit interesting band structures with tunable bandgaps. The bandgap is one of the most important factors in 2D materials for determining the properties and applications. For instance, graphene is a semimetal with zero bandgap, which limits its applications in electronics and photo-electronics. TMDCs exhibit variable bandgaps from 0 eV to 3 eV, which can be tuned by thickness[10], defects[11], dopants[12]. and mechanical deformations (by applying the tensile strain or compressive strain) [13][14]. The most studied semiconducting TMDCs (e.g., MoS_2, $MoSe_2$, WS_2, WSe_2) have shown typical features in electronic structures. The bandgap increases with the decreasing thickness and it possesses the transition from indirect in the bulk crystals to direct in the monolayers[10][15]. For instance, the indirect bandgap of -1.29 eV will be changed to a direct bandgap of -1.8 eV when bulk MoS_2 is down to a monolayer[16].

Benefiting from their unique crystal structures and electronic structures, TMDCs have shown great potential in various fields, including electronics/optoelectronics[1][17] , catalysis[18] , energy storage[19] and conversion[20] , sensing[21][22] and so on. The application of TMDCs in pollution reduction is a compelling research topic. The increasing environmental pollution issue has been one of the serious problems in the earth. Enormous efforts have been made to search the efficient and low-cost methods for addressing the environmental pollution issue. TMDCs may be a kind of promising materials for tacking these problems with several advantages. Firstly, TMDCs have a high surface-to-volume ratio. They offer more effective active sites on the surface, as well as abundant unsaturated surface sites. Thus, the layered TMDCs are excellent platforms for the anchor of semiconductor nanoparticles in various photocatalytic applications[23][24] . Due to their high surface-to-volume ratio, TMDCs are extremely sensitive to the surrounding atmosphere and can be utilized in toxic gas sensing and adsorption. Secondly, TMDCs have tunable bandgaps, which enhances the photocatalytic performance in nanocomposite by offering appropriate bandgap and band alignment [25]. Thirdly, defect engineering can be easy to implement in 2D materials, which have been confirmed to be an efficient method for intensifying the catalytic activities in TMDCs[26][27][28][29]. Lastly but importantly, there is a large variety for TMDCs (about 40 kinds) and they have an abundant amount in nature or can be synthesized [9]. So far, MoS_2, WS_2, $MoSe_2$ and ReS_2 have been naturally found[30] [31][32]. Specifically, MoS_2 exists as molybdenite in nature and is the main source of molybdenum with a large amount [33]. The main metals (W and Mo) in TMDCs are both abundant, cheap and widely used in industry[34]. TMDCs can be prepared by using various techniques, such as chemical vapour deposition (CVD)[35][36] , chemical vapour transport(CVT) [37][38], flux growth method[39], hydrothermal synthesis[40], Langmuir−Schaefer deposition[41], etc. In addition, the top-down exfoliated method can be also used to fabricate few-layer TMDCs from bulk crystals, e.g. mechanical exfoliations, liquid phase exfoliations[42][43][44]. With increasing interests in TMDCs for applications, we aim to prepare an overview of the recent progress of TMDCs in reducing the environmental pollution. We will summarize the representative efforts, including gas adsorption and removal, gas sensing, wastewater treatment, fuel cleaning, CO_2 valorisation and conversion.

In summary, this work reviews the recent advanced work of TMDCs in applications of pollution reduction. The unique and exclusive features of TMDCs (e.g., layered structure, tunable bandgap, unique optical, thermal and electrical properties, etc.) have been the main driving force that drives the researchers’ attention on exploring the potential of the 2D materials in pollution reduction applications. This work summarises the state-of-the-art applications of various TMDCs under the context of pollution mitigation (include (i) gas adsorption and removal, (ii) gas sensing, (iii) wastewater treatment, (iv) flue cleaning and (v) CO_2 valorisation and conversion). In addition to the up-to-date progress of TMDCs research, this article also discusses some of the key challenges for the future commercialisation of TMDC materials. Apparently, many of the reviewed research works have authenticated their substantial potential to substitute the existing pollution mitigation media. Nevertheless, the current applications are still restricted to lab basis, where the deviation of the actual performance of TMDCs under larger-scale production remains as the research gap. To usher TMDCs into the next level of utilization (i.e., from lab scale to industrial scale), the following three research directions should be followed up, (i) techno-economic analysis (TEA) study; (ii) experimentation under more rigorous and realistic conditions and (iii) experimental optimization for application purpose.

References

1. B. Radisavljevic; A. Radenovic; J. Brivio; V. Giacometti; Andras Kis; Single-layer MoS2 transistors. *Nature Nanotechnology* **2011**, *6*, 147-150, 10.1038/nnano.2010.279.
2. Zongyou Yin; Hai Li; Hong Li; Lin Jiang; Yumeng Shi; Yinghui Sun; Gang Lu; Qing Zhang; Xiaodong Chen; Hua Zhang; et al. Single-Layer MoS2 Phototransistors. *ACS Nano* **2011**, *6*, 74-80, 10.1021/nn2024557.
3. K. F. Mak; Kathryn McGill; J. Park; Paul L. McEuen; The valley Hall effect in MoS2 transistors. *Science* **2014**, *344*, 1489-1492, 10.1126/science.1250140.
4. Haoyi Li; Xiaofan Jia; Qi Zhang; Xun Wang; Metallic Transition-Metal Dichalcogenide Nanocatalysts for Energy Conversion. *Chem* **2018**, *4*, 1510-1537, 10.1016/j.chempr.2018.03.012.
5. Yong Ping Gao; Xu Wu; Ke-Jing Huang; Ling-Li Xing; Ying-Ying Zhang; Lu Liu; Two-dimensional transition metal diseleniums for energy storage application: a review of recent developments. *CrystEngComm* **2017**, *19*, 404-418, 10.1039/c6ce02223e.
6. J. M. Lü; O. Zheliuk; I. Leermakers; N. F. Q. Yuan; U. Zeitler; K. T. Law; Jianting Ye; Evidence for two-dimensional Ising superconductivity in gated MoS2. *Science* **2015**, *350*, 1353-1357, 10.1126/science.aab2277.
7. Xiangjun Liu; Yong-Wei Zhang; Thermal properties of transition-metal dichalcogenide. *Chinese Physics B* **2018**, *27*, 034402, 10.1088/1674-1056/27/3/034402.
8. Rajesh Kappera; Damien Voiry; Sibel Ebru Yalcin; Brittany Branch; Gautam Gupta; Aditya D. Mohite; Manish Chhowalla; Phase-engineered low-resistance contacts for ultrathin MoS2 transistors. *Nature Materials* **2014**, *13*, 1128-1134, 10.1038/nmat4080.
9. Kolobov, A. V.; Tominaga, J.. Two-Dimensional Transition-Metal Dichalcogenides; Springer International Publishing: Switzerland,; Springer International Publishing: Switzerland, 2016; pp. 32.

10. Qing Hua Wang; Kourosh Kalantar-Zadeh; Andras Kis; Jonathan N. Coleman; Michael S. Strano; Electronics and optoelectronics of two-dimensional transition metal dichalcogenides. *Nature Nanotechnology* **2012**, *7*, 699-712, 10.1038/nnano.2012.193.

11. Santosh Kc; Roberto C. Longo; Rafik Addou; Robert M. Wallace; Kyeongjae Cho; Impact of intrinsic atomic defects on the electronic structure of MoS2monolayers. *Nanotechnology* **2014**, *25*, 375703, 10.1088/0957-4484/25/37/375703.

12. Simin Feng; Zhong Lin; Xin Gan; Ruitao Lv; Mauricio Terrones; Doping two-dimensional materials: ultra-sensitive sensors, band gap tuning and ferromagnetic monolayers.. *Nanoscale Horizons* **2017**, *2*, 72-80, 10.1039/c6nh00192k.

13. Mahdi Ghorbani-Asl; S. Borini; Agnieszka B. Kuc; Thomas Heine; Strain-dependent modulation of conductivity in single-layer transition-metal dichalcogenides. *Physical Review B* **2013**, *87*, 235434, 10.1103/physrevb.87.235434.

14. Xiangying Su; Weiwei Ju; Yongliang Yong; Ruizhi Zhang; Chongfeng Guo; Jiming Zheng; Xiaohong Li; Bandgap engineering of MoS 2 /MX 2 (MX 2 = WS 2 , MoSe 2 and WSe 2) heterobilayers subjected to biaxial strain and normal compressive strain. *RSC Advances* **2016**, *6*, 18319-18325, 10.1039/C5RA27871F.

15. Julia Gusakova; Xingli Wang; Li Lynn Shiau; Anna Krivosheeva; Victor Shaposhnikov; Victor Borisenko; Vasilii Gusakov; Beng Kang Tay; Electronic Properties of Bulk and Monolayer TMDs: Theoretical Study Within DFT Framework (GVJ-2e Method). *physica status solidi (a)* **2017**, *214*, 1700218, 10.1002/pssa.201700218.

16. Kin Fai Mak; Changgu Lee; James Hone; Jie Shan; Tony F. Heinz; Atomically Thin MoS2 : A New Direct-Gap Semiconductor. *Physical Review Letters* **2010**, *105*, 136805, 10.1103/physrevlett.105.136805.

17. Muharrem Acerce; Damien Voiry; Manish Chhowalla; Metallic 1T phase MoS2 nanosheets as supercapacitor electrode materials. *Nature Nanotechnology* **2015**, *10*, 313-318, 10.1038/nnano.2015.40.

18. Hui Li; Yongwen Tan; Pan Liu; Chenguang Guo; Min Luo; Jiuhui Han; Tianquan Lin; Fuqiang Huang; Mingwei Chen; Atomic-Sized Pores Enhanced Electrocatalysis of TaS 2 Nanosheets for Hydrogen Evolution. *Advanced Materials* **2016**, *28*, 8945-8949, 10.1002/adma.201602502.

19. Tyler Stephenson; Zhi Li; Brian Olsen; David Mitlin; Lithium ion battery applications of molybdenum disulfide (MoS2) nanocomposites. *Energy & Environmental Science* **2014**, *7*, 209-231, 10.1039/c3ee42591f.

20. Yung-Huang Chang; Cheng-Te Lin; Tzu-Yin Chen; Chang-Lung Hsu; Yi-Hsien Lee; Wenjing Zhang; Kung-Hwa Wei; L.-J. Li; Highly Efficient Electrocatalytic Hydrogen Production by MoSxGrown on Graphene-Protected 3D Ni Foams. *Advanced Materials* **2012**, *25*, 756-760, 10.1002/adma.201202920.

21. Padmanathan Karthick Kannan; Dattatray Late; Hywel Morgan; Chandra Sekhar Rout; Recent developments in 2D layered inorganic nanomaterials for sensing. *Nanoscale* **2015**, *7*, 13293-13312, 10.1039/c5nr03633j.

22. Yongfu Sun; Shan Gao; Fengcai Lei; Yi Xie; Atomically-thin two-dimensional sheets for understanding active sites in catalysis. *Chemical Society Reviews* **2015**, *44*, 623-636, 10.1039/c4cs00236a.

23. Yuanhua Sang; Zhenhuan Zhao; Mingwen Zhao; Pin Hao; Yanhua Leng; Hong Liu; From UV to Near-Infrared, WS2Nanosheet: A Novel Photocatalyst for Full Solar Light Spectrum Photodegradation. *Advanced Materials* **2014**, *27*, 363-369, 10.1002/adma.201403264.

24. Paul Atkin; Torben Daeneke; Yichao Wangc; B. J. Carey; K. J. Berean; R. M. Clark; Jian Zhen Ou; A. Trinchi; Ivan Cole; Kourosh Kalantar-Zadeh; et al. 2D WS 2 /carbon dot hybrids with enhanced photocatalytic activity. *Journal of Materials Chemistry A* **2016**, *4*, 13563-13571, 10.1039/C6TA06415A.

25. Jun Di; Jiexiang Xia; Yuping Ge; Li Xu; Hui Xu; Jun Chen; Minqiang He; Huaming Li; Facile fabrication and enhanced visible light photocatalytic activity of few-layer MoS 2 coupled BiOBr microspheres. *Dalton Transactions* **2014**, *43*, 15429-15438, 10.1039/c4dt01652a.

26. Thomas F. Jaramillo; Kristina P. Jørgensen; Jacob Lindner Bonde; Jane Hvolbæk Nielsen; Sebastian Horch; Ib Chorkendorff; Identification of Active Edge Sites for Electrochemical H2 Evolution from MoS2 Nanocatalysts. *Science* **2007**, *317*, 100-102, 10.1126/science.1141483.

27. Bishnupad Mohanty; Mahdi Ghorbani-Asl; Silvan Kretschmer; Arnab Ghosh; Puspendu Guha; Subhendu K Panda; Bijayalaxmi Jena; Arkady V. Krasheninnikov; Bikash Kumar Jena; MoS2 Quantum Dots as Efficient Catalyst Materials for the Oxygen Evolution Reaction. *ACS Catalysis* **2018**, *8*, 1683-1689, 10.1021/acscatal.7b03180.

28. Gonglan Ye; Yongji Gong; Junhao Lin; Bo Li; Yongmin He; Sokrates T. Pantelides; Wu Zhou; Robert Vajtai; Pulickel M. Ajayan; Defects Engineered Monolayer MoS2 for Improved Hydrogen Evolution Reaction. *Nano Letters* **2016**, *16*, 1097-1103, 10.1021/acs.nanolett.5b04331.

29. Karen Chan; Charlie Tsai; Heine Anton Hansen; Jens Nørskov; Molybdenum Sulfides and Selenides as Possible Electrocatalysts for CO 2 Reduction. *ChemCatChem* **2014**, *6*, 1899-1905, 10.1002/cctc.201402128.

30. T. Jade Mohajerin; George R. Helz; Karen H. Johannesson; Tungsten–molybdenum fractionation in estuarine environments. *Geochimica et Cosmochimica Acta* **2016**, *177*, 105-119, 10.1016/j.gca.2015.12.030.
31. Zhi Ren; Taofa Zhou; Pete Hollings; Noel C. White; Fangyue Wang; Feng Yuan; Peter Hollings; Trace element geochemistry of molybdenite from the Shapinggou super-large porphyry Mo deposit, China. *Ore Geology Reviews* **2018**, *95*, 1049-1065, 10.1016/j.oregeorev.2018.02.011.
32. Joshua Golden; Melissa McMillan; Robert T. Downs; Grethe Hystad; Ian Goldstein; Holly Stein; Aaron Zimmerman; Dimitri A. Sverjensky; John T. Armstrong; Robert Hazen; et al. Rhenium variations in molybdenite (MoS2): Evidence for progressive subsurface oxidation. *Earth and Planetary Science Letters* **2013**, *366*, 1-5, 10.1016/j.epsl.2013.01.034.
33. Martin Pumera; Zdeněk Sofer; Adriano Ambrosi; Layered transition metal dichalcogenides for electrochemical energy generation and storage. *Journal of Materials Chemistry A* **2014**, *2*, 8981-8987, 10.1039/c4ta00652f.
34. Ali Eftekhari; Tungsten dichalcogenides (WS2, WSe2, and WTe2): materials chemistry and applications. *Journal of Materials Chemistry A* **2017**, *5*, 18299-18325, 10.1039/c7ta04268j.
35. Yongjie Zhan; Zheng Liu; Sina Najmaei; Pulickel M. Ajayan; Jun Lou; Large-Area Vapor-Phase Growth and Characterization of MoS2Atomic Layers on a SiO2Substrate. *Small* **2012**, *8*, 966-971, 10.1002/smll.201102654.
36. Qingqing Ji; Cong Li; Jingli Wang; Jingjing Niu; Yue Gong; Yanfeng Zhang; Qiyi Fang; Yu Zhang; Jianping Shi; Lei Liao; et al. Metallic Vanadium Disulfide Nanosheets as a Platform Material for Multifunctional Electrode Applications. *Nano Letters* **2017**, *17*, 4908-4916, 10.1021/acs.nanolett.7b01914.
37. J.A. Wilson; A.D. Yoffe; The transition metal dichalcogenides discussion and interpretation of the observed optical, electrical and structural properties. *Advances in Physics* **1969**, *18*, 193-335, 10.1080/00018736900101307 10.1080/00018736900101307.
38. Alberto Ubaldini; Jacim Jacimovic; Nicolas Ubrig; Enrico Giannini; Chloride-Driven Chemical Vapor Transport Method for Crystal Growth of Transition Metal Dichalcogenides. *Crystal Growth & Design* **2013**, *13*, 4453-4459, 10.1021/cg400953e.
39. Xixia Zhang; Fei Lou; Chunlong Li; Xiang Zhang; Ning Jia; Tongtong Yu; Jingliang He; Baitao Zhang; Haibing Xiab; Shanpeng Wang; et al. Flux method growth of bulk MoS2single crystals and their application as a saturable absorber. *CrystEngComm* **2015**, *17*, 4026-4032, 10.1039/c5ce00484e.
40. Lijuan Ye; Haiyan Xu; Dingke Zhang; Shijian Chen; Synthesis of bilayer MoS2 nanosheets by a facile hydrothermal method and their methyl orange adsorption capacity. *Materials Research Bulletin* **2014**, *55*, 221-228, 10.1016/j.materresbull.2014.04.025.
41. Anna Kálosi; Maksym Demydenko; Michal Bodik; Jakub Hagara; Mario Kotlar; Dmytro Kostiuk; Yuriy Halahovets; Karol Vegso; Alicia Marin Roldan; Gulab Singh Maurya; et al. Tailored Langmuir–Schaefer Deposition of Few-Layer MoS2 Nanosheet Films for Electronic Applications. *Langmuir* **2019**, *35*, 9802-9808, 10.1021/acs.langmuir.9b01000.
42. Xiao Huang; Zhiyuan Zeng; Hua Zhang; Metal dichalcogenide nanosheets: preparation, properties and applications. *Chemical Society Reviews* **2013**, *42*, 1934, 10.1039/c2cs35387c.
43. Hai Li; Jumiati Wu; Zongyou Yin; Hua Zhang; Preparation and Applications of Mechanically Exfoliated Single-Layer and Multilayer MoS2 and WSe2 Nanosheets. *Accounts of Chemical Research* **2014**, *47*, 1067-1075, 10.1021/ar4002312.
44. Graeme Cunningham; Mustafa Lotya; Clotilde Cucinotta; S. Sanvito; Shane D. Bergin; Robert Menzel; M.S.P. Shaffer; Jonathan N. Coleman; Solvent Exfoliation of Transition Metal Dichalcogenides: Dispersibility of Exfoliated Nanosheets Varies Only Weakly between Compounds. *ACS Nano* **2012**, *6*, 3468-3480, 10.1021/nn300503e.
45. Hai Li; Jumiati Wu; Zongyou Yin; Hua Zhang; Preparation and Applications of Mechanically Exfoliated Single-Layer and Multilayer MoS2 and WSe2 Nanosheets. *Accounts of Chemical Research* **2014**, *47*, 1067-1075, 10.1021/ar4002312.
46. Graeme Cunningham; Mustafa Lotya; Clotilde Cucinotta; S. Sanvito; Shane D. Bergin; Robert Menzel; M.S.P. Shaffer; Jonathan N. Coleman; Solvent Exfoliation of Transition Metal Dichalcogenides: Dispersibility of Exfoliated Nanosheets Varies Only Weakly between Compounds. *ACS Nano* **2012**, *6*, 3468-3480, 10.1021/nn300503e.