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Layered Transition Metal Dichalcogenides for Electrochemical Energy Generation and Storage

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Layered transition metal dichalcogenides (TMDs) (MoS\textsubscript{2}, MoSe\textsubscript{2}, WS\textsubscript{2}, WSe\textsubscript{2}, etc.) are a chemically diverse class of compounds having band gaps from 0 to ~2 eV and remarkable electrochemical properties. The band gaps and electrochemical properties of TMDs can be tuned by exchanging the transition metal or chalcogenide elements. After a brief description of the most commonly followed synthetic routes to prepare TMDs, we wish to highlight in this review the diverse electrochemical applications of MoS\textsubscript{2}, a representative and well-studied TMD, which span from its use as catalysts in hydrogen evolution reactions to its adoption in supercapacitors, batteries, solar cells, and hydrogen storage.

1. Introduction

Transition metal dichalcogenides (TMD) are scientifically interesting and industrially important compounds. Chalcogenides, that is S, Se, and Te (VI A group), create very stable binary compounds with transition elements forming layered crystalline structures especially with transition metals of group IV-VII B. Their layered structure resembles that of graphite with weak van der Waals interactions between the individual layers. The crystal structure varies from the hexagonal P6\textsubscript{3}/mmc for molybdenite (MoS\textsubscript{2}) and tungstenite (WS\textsubscript{2}) to the orthorhombic structure Pmn2\textsubscript{1}, as for MoTe\textsubscript{2} and WTe\textsubscript{2}, giving rise to dramatic anisotropy and different material properties (see Figure 1). Such properties are of industrial importance. For example, due to their layered structure, MoS\textsubscript{2} and WS\textsubscript{2} can be employed as dry lubricants able to withstand higher temperatures than graphite.\textsuperscript{1} Layered transition metal dichalcogenides are compounds of the general formula MX\textsubscript{2} where M is a transition element of groups IV B (Ti, Zr, Hf), V B (V, Nb, Ta), VI B (Mo, W), and VII B (Tc, Re) and X is a chalcogen atom of the VI A group (S, Se, Te). VIII B group elements create dichalcogenides, which in some cases are partially layered in structure (Co, Ni; Rh, Pd, Ir, Pt). Unlike pristine graphene, which is a semimetal with a zero band gap, TMDs exhibit a variable band gap between 0 (semimetal) to 2 eV (semiconducting) depending on the element combination, the number of layers, and the presence or lack of a doping atom. TMDs exhibit well-defined structures, unlike doped graphene, which loses its crystalline structure when covalently doped to tune its bandgap, effectively creating poorly defined amorphous graphenoid material.\textsuperscript{2} Tuning of the band gap is important for electronic, electrochemical, and optical applications of these layered binary materials. Layered TMDs also possess catalytic properties, which can easily be tuned with selective doping. For example, MoS\textsubscript{2} doped with Co or Ni is used in the petrochemical industry for hydrodesulfurization processes.\textsuperscript{3,4} MoS\textsubscript{2} is found as the mineral molybdenite (mined i.e., in Norway, Australia, and North America). Some other TMDs are known from nature: WS\textsubscript{2} (tungstenite), MoSe\textsubscript{2} (drysdallite), ReS\textsubscript{2} (rhenite). However, only molybdenite, which is the main source of molybdenum, is found in nature in large amounts. Molybdenite can form large crystals in some types of geological formations (for example, granite pegmatite veins, cracks in granite and granodiorite, quartz-MoS\textsubscript{2}-Bi veins, Sn-W greisen veins, Sn-Cu greisen veins, and disseminated porphyry with Cu-Mo and Mo mineralization). Naturally occurring crystals of MoS\textsubscript{2} have sufficient quality for basic research applications. The natural crystals of molybdenite and tungstenite are shown in Figure 2. The layered structure of TMDs offers the possibility of preparing well-defined ultra-thin structures and, ultimately, single layers, which possess remarkably different electronic properties than those of their counterpart bulk materials. Such tunability properties make them ideal materials for electronic or electrochemical devices. With increasing interest in layered TMDs from the research community, we wish to provide focused minireview on the representative past efforts in the use of layered TMDs in electrochemical applications. We will describe the electrochemical applications of layered TMDs from bulk materials to single-layer sheets. We hope to provide here introduction of the field to chemists and materials scientists who are new to the field as well as to provide useful discussion of the key papers to the experts. We wish to direct interested readers to more specific reviews; there are excellent extensive review articles focused on the structure and interfacial properties of bulk TMDs,\textsuperscript{5} on the use of TMDs in lithium batteries,\textsuperscript{6} general materials properties of nanosized TMDs,\textsuperscript{7} and energy storage and conversion devices.\textsuperscript{8,9}
and W. As the sulfur source, thiols or dialkyl sulfides and dialkyl selenides\(^{18-21}\) are usually used. The bulk synthesis of TMD nanostructures is based on the reaction of sulfur precursors (such as Na\(_2\)S, CH\(_3\)CSNH\(_2\), NH\(_2\)CSNH\(_2\), KSCN) with molybdate ions.\(^{22\,\text{a}}\) Another strategy for the “bottom-up” synthesis of TMDs is based on the thermal decomposition and subsequent reduction of thiomolybdates or thiotungstenates under hydrothermal conditions.\(^{15}\)

### 3. Electrochemical properties

#### 3.1. Photoelectrochemistry

Interesting photoelectrochemical properties were found in thin films of MoS\(_2\) and MoSe\(_2\). Ultrathin MoS\(_2\) sheets (thickness of 39 nm) were found to exhibit poor heterogeneous electron transfer (HET) rates (low \(k^0\)) and low faradic currents in dark environments for non-aqueous electrochemistry in acetonitrile. Upon white light irradiation, the HET rates increased dramatically for all tested compounds such as decamethylferrocene and tetrachlorobenzoquinone, tetracyanoquinodimethane (TCNQ), and tetramethylphenylenediamine (TMPD).\(^{23}\) Similar photoelectrochemical behavior was observed for MoSe\(_2\) bulk materials (see Figure 4).\(^{24\,\text{a}}\) Photoelectrochemical oxidation of Cl\(^-\) and Br\(^-\) on bulk MoS\(_2\) and WS\(_2\) in the production of Cl\(_2\) and Br\(_2\) was investigated. Platinitized TMD showed enhanced performance than did bare layered MoS\(_2\) and WS\(_2\).\(^{25}\) It was shown theoretically and experimentally that there are qualitative differences in the photoelectrochemistry of bulk and nanostructured MoS\(_2\).\(^{26}\)

#### 3.2. Hydrogen evolution reaction

Layered TMDs are immensely popular for use in electrochemical hydrogen evolution reactions (HER).\(^{27}\) It was contended that the edge planes of MoS\(_2\) are the active sites for HER.\(^{28}\) It was found that current density during HER scales directly with exposed edge sites of MoS\(_2\)\(^{29}\) and that changing the dimensions of MoS\(_2\) from bulk sizes to single-layer structures leads to special surface properties that can greatly improve material HER performance.\(^{26\,\text{a}}\)
In contrast, other groups found that there is very little difference between bulk and ultrathin films of MoS$_2$ for HER.\textsuperscript{30} It was shown that metallic single layer 1T-MoS$_2$ polymorph exhibits highly favorable HER properties.\textsuperscript{31} Doping bulk MoS$_2$ with other transition metals was found to tune the reduction potential towards H\textsuperscript{+}.\textsuperscript{32} MoS$_2$ was found to be beneficial as an electrode material for HER in microbial electrolysis cells to replace Pt.\textsuperscript{33} Few-layer MoS$_2$ sheets were synthesized on carbon nanospheres and used for HER.\textsuperscript{34} In order to combine the catalytic properties of MoS$_2$ nanostructured materials with the favorable electrical properties of carbon materials, systems with enhanced performance have recently been obtained by synthesizing MoS$_2$ nanostructures over carbon nanotubes\textsuperscript{35} and graphene.\textsuperscript{36} Specifically, the solvothermal synthesis of MoS$_2$ in the presence of reduced graphene generated a composite with a high concentration of edge-plane structures of MoS$_2$, which generated an overpotential as small as ~0.1 V.\textsuperscript{37}

MoS$_2$ nanoparticles (of 1.47 nm) were deposited on an Au electrode and exhibited favorable HER properties.\textsuperscript{37} In other work, MoS$_2$ deposited on 3D Ni foam was reported to be highly efficient in HER.\textsuperscript{38} Core-shell MoO$_3$/MoS$_2$ nanotube arrays exhibited highly efficient hydrogen evolution due to the high surface area.\textsuperscript{39} Research on hydrogen evolution is theoretically well supported. It was shown that MoS$_2$ exhibits much more favorable reaction coordinates for H$_2$ evolution than do many other catalysts and is similar to those of the hydrogenase and nitrogenase enzymes (Figure 5).\textsuperscript{40} MoS$_2$ particles (non-layered structure) were shown to demonstrate lower reduction potentials (that is, more favourable) than MoS$_2$ microcrystals.\textsuperscript{41} In depth review on the HER on MoS$_2$ can be found in Ref.\textsuperscript{42}

Strained single-sheet WS$_2$ were prepared by chemical exfoliation and exhibited very high catalytic activity towards HER.\textsuperscript{43} MoS$_2$ can act as enhancer of photocatalyst efficiency. CdSe nanoribbons are photocatalytic materials capable of induction of H$_2$ evolution from aqueous solution. When MoS$_2$ was linked to CdSe nanoribbons, the efficiency of the composite material increased about 4 times due to the participation of MoS$_2$ in hydrogen reduction. Interestingly, CdSe-Pt hybrids showed lower performance than CdSe-MoS$_2$ hybrids.\textsuperscript{44}
3.3. Capacitive behaviour

Since MoS$_2$ has a layered structure similar to graphite, it exhibits two key crystal features: a basal plane and an edge plane. The edge plane of MoS$_2$ has been found to be more electroactive. To create a surface with high-energy storage capacity, edge-oriented nanowall films were fabricated by chemical vapor deposition (Figure 6). It was found that MoS$_2$ nanowall films exhibited excellent supercapacitor properties, similar to those of carbon nanotubes.\textsuperscript{45} Spray painting of MoS$_2$ with consequent laser patterning was developed for the construction of micro-supercapacitors which exhibited the high area capacitance of 8 mF cm$^{-2}$.\textsuperscript{46} Recently, porous tubular C/MoS$_2$ composites have been fabricated using anodic aluminum oxide film as template. The capacitor assembled using this nanocomposite material exhibited good gravimetric capacitance of 210 mF g$^{-1}$ and excellent cycling stability.\textsuperscript{47}

3.4. Batteries

Layered TMDs, especially MoS$_2$, is used in lithium batteries as anodes. It was shown that hollow MoS$_2$ particles have better stability than do solid MoS$_2$ nanoparticles.\textsuperscript{48} MoS$_2$ composites layered with graphene exhibited highly stable cycling performance and a high specific capacity of $\sim$1100 mAh/g at a current of 100 mA/g\textsuperscript{49} and 350 mA h/g at a current of 2000 mA/g.\textsuperscript{50} Three-dimensional MoS$_2$ flower-like nanoarchitectures anchored on graphene layers were prepared via the hydrothermal route. Such MoS$_2$ nanoflowers resulted in the highly spaced MoS$_2$ nanosheets (spacing 13.8 Å, compare to bulk MoS$_2$ with spacing of 6.2 Å), which was useful for the intercalation of Li$^+$ ions. This material has capacity of 813.5 mAh/g at a current density of 1000 mA/g. It was found that it was possible to achieve specific capacity of 600 mA/h/g even at a high current density of 4000 mA/g.\textsuperscript{51} An interesting approach was taken to provide sulfur in lithium-sulfur batteries. To avoid the instability of Li$_2$S, a mixture of elemental Li and MoS$_2$ was electrochemically converted to Li$_2$S and elemental Mo. The authors claim that the resulting cell has very high stability.\textsuperscript{52} In a manner similar to Ref [50], where MoS$_2$ and graphene were utilized, composites of MoS$_2$ with single-walled carbon nanotubes and MoS$_2$ nanorods coated by amorphous carbon exhibited very high capacity in Li batteries: 992 mAh/g\textsuperscript{53} and 621 mAh/g.\textsuperscript{54} Mesoporous WS$_2$ was also used as an electrode in Li batteries.\textsuperscript{55} MoS$_2$/carbon composites are used in rechargeable Mg batteries.\textsuperscript{56} The layered structure of bulk MoS$_2$ was found to be an attractive material for novel Na$^+$ batteries.\textsuperscript{57}

3.5. Solar cells

TMDs can play several roles in solar cell energy conversion. The TiO$_2$ used in solar cells can be sensitized by WS$_2$ nanosheets, resulting in much better performance than non-sensitized TiO$_2$.\textsuperscript{58} The authors found that the S-W-S layers of WS$_2$ are not perfectly aligned in the direction of the c-axis, emphasizing the role of lateral electron transfer. Another way to sensitize TiO$_2$ is the use of organic dyes.\textsuperscript{59} WS$_2$ has been found to be very useful for replacement of Pt in dye-sensitized solar cells.\textsuperscript{60} MoS$_2$/graphene nanocomposite was used as counter electrode in dye-sensitized solar cells with high power conversion efficiency of $\sim$6%.\textsuperscript{61}

In such cases, TMDs are used as replacements of the limiting factor of such cells, the counter electrode, which typically uses a Pt catalyst on a conductive support. MoS$_2$ films on a carbon support were suggested as Pt-free counter electrodes in dye-sensitized solar cells.\textsuperscript{52} Similarly, MoS$_2$ nanosheets were deposited on multiwall carbon nanotubes and used as a replacement for Pt in solar cells.\textsuperscript{63}

3.6. Other electrochemical energy applications

Electrochemical hydrogen storage in MoS$_2$ nanotubes was reported, up to 0.97% wt. of H$_2$.\textsuperscript{64} Such adsorption was reported from the electrochemical reduction of water according to eq. (1)
Later, the same authors improved the hydrogen storage capacity by up to 1.2% wt. by treating MoS$_2$ nanotubes with KOH. It should be noted that as a control material, polycrystalline MoS$_2$ was used and exhibited a hydrogen storage capacity of <0.3% wt.$^{55}$

**Conclusions**

Layered transition metal dichalcogenides exhibit tunable band gap properties, interesting photoelectrochemistry, and versatile applications for hydrogen reduction, supercapacitors, batteries, and solar cells. Layered TMDs exhibit crystalline structure and their electrochemical properties can be tuned by exchanging transition metal or chalcogenide atoms. It can be expected that there will be a dramatic increase in the number of applications of these two-dimensional materials in electrochemistry.

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**Biography**

**Prof. Martin Pumera** is a faculty member at Nanyang Technological University, Singapore since 2010. He received his PhD at Charles University, Czech Republic, in 2001. After two postdoctoral stays (in the USA, Spain), he joined the National Institute for Materials Science, Japan, in 2006 for a tenure-track arrangement and stayed there until Spring 2008 when he accepted a tenured position at NIMS. In 2009, Prof. Pumera received a ERC-StG award. Prof. Pumera has broad interests in nanomaterials and microsystems, in the specific areas of electrochemistry and synthetic chemistry of 2D nanomaterials, nanomotors, nanotoxicity, and energy storage devices. He is associate editor of Science and Technology of Advanced Materials, member of Editorial board of Chem. Eur. J., Electrochem. Commun., Electrophoresis, Electroanalysis, The Chemical Records, ChemElectroChem and eight other journals. He published over 250 peer-reviewed articles and has h-index 43.

**Assoc. Prof. Zdeněk Sofer** is a faculty member at Institute of Chemical Technology Prague, Czech Republic since 2008. He received his PhD at Institute of Chemical Technology Prague, Czech Republic in 2008. He was visiting scientist at Forschungszentrum Jülich, Germany (2004-2005) and at Universität Duisburg-Essen, Germany (2009). Assoc. Prof. Sofer received a rector award for young talented scientists in 2013. Assoc. Prof. Sofer research interests lie in the area of 2-dimensional nanomaterials and wide band-gap semiconductors. He published over 75 peer-reviewed articles and has h-index 11.

**Dr. Adriano Ambrosi** received his PhD degree from Dublin City University, Ireland in 2007. As postdoctoral researcher he firstly worked for two years at ICN (Spain), and then, in 2009, at NIMS (Japan). In 2010 he joined the research group of Prof. Martin Pumera at Nanyang Technological University (Singapore) where he currently works as Senior Research Fellow. His research interests include the application of nanomaterials to electrochemical biosensors, synthesis and fundamental electrochemical studies of graphene and other 2D materials for biosensing and energy storage devices, and synthetic nanomotors.

**Notes and references**

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