

Review

Nanoarchitectonics of Layered Metal Chalcogenides-Based Ternary Electrocatalyst for Water Splitting

Arunachalam Arulraj ^{1,2,*} , Praveen Kumar Murugesan ², Rajkumar C. ³ , Alejandra Tello Zamorano ⁴ and Ramalinga Viswanathan Mangalaraja ^{2,*} 

¹ Department of Physics, Faculty of Natural Sciences, University of Atacama, Copiapó 1530000, Chile

² Faculty of Engineering and Sciences, Adolfo Ibáñez University, Peñalolén, Santiago 7941169, Chile

³ Centre for High Energy Systems and Sciences (CHESS), DRDO, Hyderabad 500069, India

⁴ Department of Chemistry and Biology, Faculty of Natural Sciences, University of Atacama, Copiapó 1531772, Chile

* Correspondence: arulnanotech@gmail.com (A.A.); mangal@uai.cl (R.V.M.)

Abstract: The research on renewable energy is actively looking into electrocatalysts based on transition metal chalcogenides because nanostructured electrocatalysts support the higher intrinsic activity for both the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). A major technique for facilitating the conversion of renewable and sustainable energy is electrochemical water splitting. The aim of the review is to discuss the revelations made when trying to alter the internal and external nanoarchitectures of chalcogenides-based electrocatalysts to enhance their performance. To begin, a general explanation of the water-splitting reaction is given to clarify the key factors in determining the catalytic performance of nanostructured chalcogenides-based electrocatalysts. To delve into the many ways being employed to improve the HER's electrocatalytic performance, the general fabrication processes utilized to generate the chalcogenides-based materials are described. Similarly, to enhance the OER performance of chalcogenides-based electrocatalysts, the applied complementary techniques and the strategies involved in designing the bifunctional water-splitting electrocatalysts (HER and OER) are explained. As a conclusive remark, the challenges and future perspectives of chalcogenide-based electrocatalysts in the context of water splitting are summarized.

Keywords: chalcogenides; nanoarchitectonics; electrocatalysts; water splitting; future perspectives



Citation: Arulraj, A.; Murugesan, P.K.; C., R.; Zamorano, A.T.; Mangalaraja, R.V. Nanoarchitectonics of Layered Metal Chalcogenides-Based Ternary Electrocatalyst for Water Splitting. *Energies* **2023**, *16*, 1669. <https://doi.org/10.3390/en16041669>

Academic Editor: Nur Awanis Hashim

Received: 15 December 2022

Revised: 10 January 2023

Accepted: 3 February 2023

Published: 7 February 2023



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1. Introduction

Renewable energy sources utilization is becoming more popular in the development of next-generation energy devices. However, most of them are so dependent on seasonal and regional factors; thus, a reliable method needs to be developed to convert the unstable and surplus energy into stable energy. In recent decades, fuel-cell technology has been booming in the energy sector, which can convert hydrogen into usable electric energy and combust it directly to provide thermal energy. It is well known that a powerful energy carrier with a high energy density is supported by hydrogen (H₂), and there are numerous existing approaches to produce the energy. One of the key methods in producing H₂ among the numerous methods is water electrolysis, which offers the benefits of higher efficiency, remarkable adaptability, and almost no carbon emissions [1]. The cathodic hydrogen evolution reaction (HER) and anodic oxygen evolution reaction (OER) are two common electrolysis reaction pathways, and several electrochemical reactions take place depending upon the electrolytes used. In actuality, the thermodynamics of the water electrolysis to produce the H₂ and O₂ at standard temperature and pressure (25 °C, 1 atm) is not favored, since the operating system requires a theoretical potential of 1.23 V. Furthermore, the real-time water electrolysis involves the complicated ionic and electron transport mechanisms leading to lower efficiency and sluggish kinetics, and it necessitates a higher applied potential. Due to the above-mentioned reasons, there

will always be a significant surplus potential (or overpotential) applied compared to the theoretical potential [2]. Numerous studies have been performed to date on improving the electrolyzer efficiency and researching the reaction mechanisms to consume less energy. Generally, the kinetic barrier reduction and an increase in the reaction rate rely greatly on the development of effective electrocatalysts. It is commonly known that the acidic electrolytic medium is favored more in water-splitting compared to the alkaline medium, as it offers compactness and also a potential to run in the reversible mode (such as fuel cells) [3]. To date, the benchmarking catalyst in the water-splitting activity is from rare earth elements such as platinum (Pt), palladium (Pd), ruthenium (Ru), etc., which can exhibit nearly zero overpotential [4]. Nonetheless, the high cost and scarcity of rare earth elements as electrocatalysts limit their commercial applicability. As a result, highly effective alternative electrocatalysts with high activity, abundance, and low cost are crucial research directions in water splitting [3]. As a result, several electrocatalysts, notably those based on transition metals and composed of widely distributed elements on the earth, have been thoroughly researched for water electrolysis (OER and HER). The developed electrocatalytic materials include single metal, alloy, oxide, hydroxide, nitride, sulfide, selenide, phosphide, arsenide, telluride, sulfoarsenide, etc., and some of these were set to be the most representative [5–7]. However, their performance is still insufficient to be deployed in the pilot scaling. Thus, to boost the performance of the catalytic activity of the developed materials, the research was pursued under the direction of two general strategies. The first strategy is to deploy large-surface-area microstructured or nanostructured electrocatalysts, due to the fact that large-surfaced electrocatalysts aid in easing the necessity for high catalyst loading [8]. The second is to create composites or alloys by combining one metal with other metals, which can enhance active sites and allows reduced catalyst loading [9]. The non-homogeneous configuration of nanostructures in composites, on the other hand, limits the stability of electrocatalytic activity [10,11]. As a result, the current demand for H₂ production from water splitting is driving the search for electrolyzers (or catalytic materials) for a large-scale, sustainable, and affordable method.

In this instance, two-dimensional (2D) layered materials such as transition metal chalcogenides (TMCs) have been actively investigated as efficient catalysts in several energy-related applications, including water-splitting [7,12–15]. Non-noble TMC-based electrocatalysts such as MoS₂ [16,17], WS₂ [16,18], NiS₂ [19,20], FeS₂ [21], MoSe₂ [22,23], WSe₂ [22,24], WTe₂ [25], and their composites are considered to be promising candidates due to the exposed catalytically active sites in the atomically thin nature of 2D materials. As mentioned, the TMCs are layered materials composed of two chalcogen atoms sandwiched between the alternating sheets of transition metal atoms [26]. While the presence of van der Waals bonds (weak force) between the layered structures of TMCs allows its exfoliation for up to single layers, with the difference in oxidation degree (metal +4 and chalcogen −2) leading to the salvation of nanosheet structure by forming strong ionic bonds between the metal and the chalcogen atoms [15,27]. Additionally, the wide range of electrocatalysts as an alternative to noble rare earth can be achieved by developing binary, ternary, and quaternary TMCs by means of controlling the stoichiometric of transition metals and chalcogens.

Among them, the ternary TMCs has evidenced to be more amenable electrocatalysts by both theoretical and experimental results, suggesting the possible optimization of transition metals to fine-tune their electronic states [28,29]. The layered ternary TMCs may represent a new class of effective electrocatalysts that merits in-depth investigation since they not only open new avenues for investigating the advanced functional composites (catalysts) but also broaden and enhance the family of high-performance water splitting (HER reactions). Even though several ternary TMCs have been developed, there have only been a few sporadic studies on the electrocatalytic activity (HER), till now [30]. Additionally, their electrocatalytic process, such as the ability to pinpoint the active site, falls well short of the necessity for scientific investigation. For H₂ production, the possible identification of active sites of the electrocatalysts is a crucial one. Thus, for designing catalytic materials, it is essential to identify the activity site of the reaction with the desired structural engineering

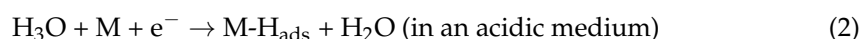
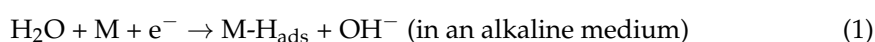
and composition. By means of such activity, it supports catalyzing the H₂ generation at a much lower onset potential with remarkable durability [31,32]. Therefore, the review aims to emphasize the main theme of nanoarchitectonics and the electrochemistry of the different layered ternary TMCs and their electrocatalytic activity in water-splitting reactions. The review focuses on this by initiating with the basic principles and electrochemistry of water splitting with its governance factors, followed by the nanoarchitectonics of the layered TMCs. A special focus has been provided for the different nanoarchitectonics describing the morphology and size-controlled structures of various TMCs and their associated electrocatalytic activities toward the production of H₂. It is important to overview the prevailing trends of the electrocatalytic activity of the layered ternary TMCs and the strategies to improve them for the water-splitting reactions. Finally, the challenges and perspectives of the ternary TMCs are presented for the development of future research directions toward water-splitting electrocatalysts.

2. Principles and Electrochemistry of Electrocatalytic Water Splitting

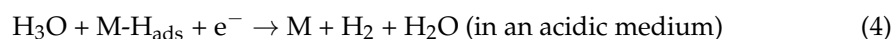
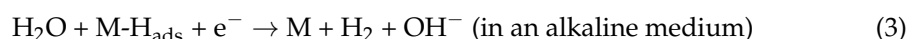
2.1. HER

The hydrogen evolution reaction (HER) is commonly recognized with a two-electron transfer involving three potential main phases with an adsorption–desorption intermediates process for the reduction of water molecules in an alkaline media (Figure 1), or protons in the acidic media, for hydrogen (H₂) production [10,33,34]. The Volmer reaction (Equations (1) and (2)) is the initial step, in which an electron and one proton adsorbed on the catalytic sites (M) react to create adsorbed hydrogen atoms (H_{ads}) on the surface of the electrocatalyst. In alkaline and acidic electrolytes, the water molecules and the hydronium cation (H₃O⁺) serve as the proton sources, respectively. The H₂ production then occurs either by the Heyrovsky reaction at low H_{ads} (Equations (3) and (4)) or the Tafel reaction at high H_{ads} coverage (Equation (5)) on the surface of the catalysts. Another proton diffuses to the H_{ads} during the Heyrovsky step, where it combines with a second electron, thereby producing H₂. In the Tafel step, H₂ is created when two nearby H_{ads} atoms join on the electrode's surface. According to mechanistic research, the H₂ originates either via the Volmer–Heyrovsky or Volmer–Tafel pathway. A series of simple steps can sum up the process of HER [35,36]:

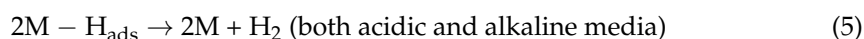
(1) Electrochemical hydrogen adsorption (Volmer reaction):



(2) Electrochemical hydrogen desorption (Heyrovsky reaction):



(3) Chemical hydrogen desorption (Tafel reaction):



The H intermediate (H*) formulation is a step in both the Volmer–Heyrovsky and Volmer–Tafel pathways. In order to evaluate the activities of HER catalysts, the ΔGH^* is considered a crucial requirement. The reaction H* should not be bound by an active catalyst that is either too weak or too strong. The overall reaction rate of the adsorption (Volmer) step will restrict if the H* binds to the surface too weakly ($\Delta\text{GH}^* > 0$), whereas the desorption (Heyrovsky/Tafel) step will limit the reaction rate if the H* binds to the surface too strongly ($\Delta\text{GH}^* < 0$) (Figure 1). Thus, the HER should possess nearly zero ΔGH^* for the ideal electrocatalyst [4,34,37]. It is crucial to create facile methods to obtain the ΔGH^* value when assessing a catalyst's HER activity. Based on density functional theory (DFT)

calculations, the recently developed computational quantum chemistry offers a suitable way to determine the ΔGH^* value. The ΔGH^* value can be calculated by simulating the potential intermediates that could occur on electrocatalyst surfaces during the HER process ($\Delta GH^* = \Delta EH^* + \Delta EZPE - T\Delta SH$). The differential hydrogen adsorption energy can be calculated by using the isolated H_2 as a reference state, the zero-point energy change ($\Delta EZPE$) for adsorbed H^* and isolated H_2 can be obtained by vibrational frequency calculation, and ΔSH is the difference in entropy between the adsorbed state and the possible intermediates formed on the surface of electrocatalysts during the HER process (T was set to be 300 K) [32]. As mentioned, DFT calculations are becoming more important in determining the ΔGH^* values as computational science and theoretical calculations are advancing. As a result, the design of volcanic relationships for different catalysts has been made possible.

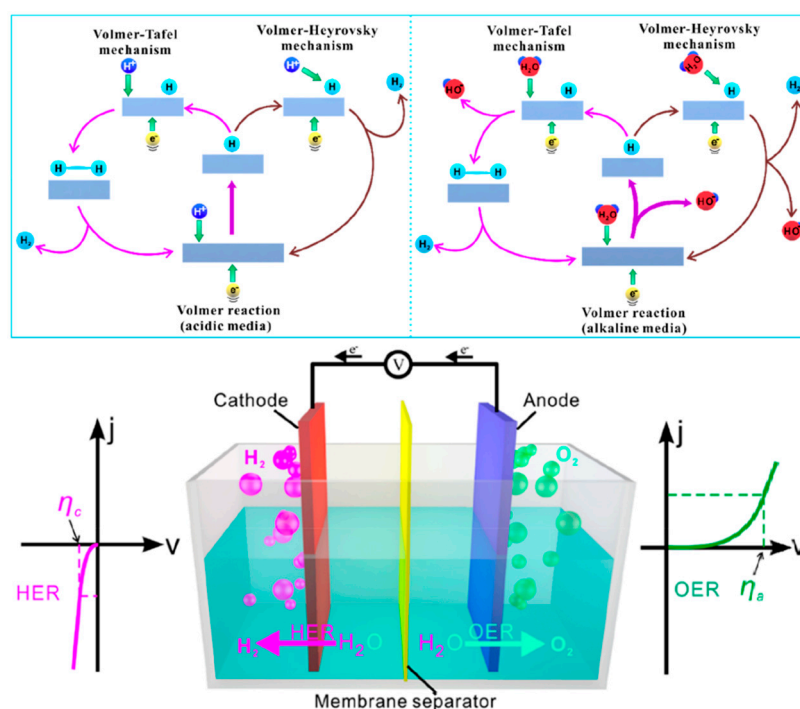
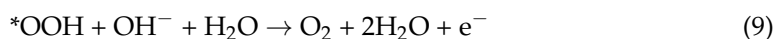
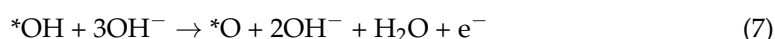


Figure 1. Schematic representation of the mechanism of H_2 evolution in acidic and alkaline conditions and water-splitting reaction [34]. Reproduced with permission from Zhu et al., Chem Rev., American Chemical Society (ACS), 2020.

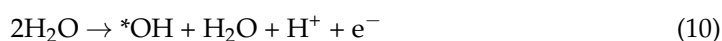
2.2. OER

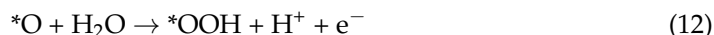
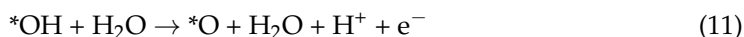
Similar to this, a four-step electron transfer process with numerous intermediates (such as *OOH , *O , and *OH) involved in the oxygen evolution reaction (OER), both in alkaline and/or acidic conditions in the reactions, is the mechanism shown in Equations (6)–(11) [38,39]:

At alkaline conditions:



At acidic conditions:





The OER's kinetics are significantly much more sluggish than those of HER, as it involves the four-electron transfer and the production of O–O bonds while serving as an indispensable half-reaction in the water-splitting process. In general, numerous electron transfers occurring simultaneously do not favor the kinetic reactions, and according to certain findings, the OER involves many phases with a single electron transfer each. For a thermodynamically ideal electrocatalyst, the total free energy variation of OER is shown to be 4.92 eV, which can be spread evenly among the four elemental stages with various adsorbates ($^*\text{OH}$, $^*\text{O}$, $^*\text{OOH}$, and O_2) [40]. The difference between the reaction intermediates $^*\text{O}$ and $^*\text{OH}$'s adsorption-free energy change is one of the universal metrics for OER. It is possible to reduce the free energy variation by placing $^*\text{O}$ in the desired location between $^*\text{OH}$ and $^*\text{OOH}$ [41].

3. Governance Index for Water Splitting (OER and HER)

Some crucial parameters can help us to evaluate the catalytic activity of the developed materials to determine whether they can be suitable to be used as electrocatalysts for water splitting. The overpotential, Tafel plots, turnover frequency, stability, and Faradaic efficiency are primarily among them [42].

3.1. Overpotential

For OER and HER catalyzing, the equilibrium potentials will be in the range of 0 and 1.23 V (both vs. RHE), respectively. However, due to the intrinsic kinetic barrier, an additional potential that is greater than the equilibrium potential is required to start the catalytic reactions of both OER and HER. Such a kind of additional potential is described to be overpotential. The electrochemical measurements using cyclic voltammetry (CV) or linear sweep voltammetry (LSV) carried out for the materials will determine the total catalytic activity. To assess the overall electrode activity, the overpotential at a specific current density is often determined. The higher electrochemical activity of the electrode is represented by a smaller value of the overpotential [43–45].

3.2. Tafel Plot

The LSV curve yields a Tafel plot, and the plot illustrates how the electrochemical kinetics link the overpotential to the rate of an electrochemical reaction. The Tafel equation, $\eta = a + b \log j$, can be used to fit the linear parts of a Tafel plot. Here, η corresponds to the overpotential, b is the Tafel slope, and j is the current density. Another measure to evaluate the intrinsic catalytic activity for water electrolysis is exchanged current density (j_0), which is the value obtained from j as a result of the Tafel equation when the applied value is zero. For the water-splitting reactions, the ideal electrocatalysts should have a modest b and a large j_0 [44,46,47].

3.3. Turnover Frequency

The number of molecular reactions that take place at the catalytic site per unit of time under specific conditions can be measured using the turnover frequency (TOF) to determine the active sites at a particular activity. TOF will be measured by applying the following Equation (14):

$$\text{TOF} = (jA)/(\alpha F n) \quad (14)$$

where j is the current density associated with the LSV results at a specific overpotential; F is the Faradaic constant ($96,485.3 \text{ C mol}^{-1}$); and n is the moles (mol) of covered metal atoms on the electrode, and is calculated from mass (g) divided by the molality

(g mol^{-1}). A is the working electrode surface area; α stands for the catalyst electron number ($\text{electrons mol}^{-1}$) [44,48].

3.4. Stability

Stability is a significant metric that is used to assess catalysts' capacity to withstand specified or durable (long-term) working conditions. There are typically two ways to assess the catalytic stability: (i) LSV measurement after performing 1000 CV cycles, and (ii) chronopotentiometry or chronoamperometry. A robust catalyst never exhibits significant changes in potential or current density over the extended operation [46].

3.5. Faradaic Efficiency

The term "faradaic efficiency" refers to the effectiveness of electron transmission in a system that facilitates an electrochemical process such as OER and/or HER in water-splitting reactions. The faradaic efficiency can be obtained by comparing the experimental and pre-determined computational (theoretical) results of the produced gas (O_2 or H_2). The gas chromatography (GC) measurements or the water displacing method can be used to calculate the amount of generated gas (H_2 or O_2). Additionally, a rotating ring disc (RRD) electrode voltammetry will also be used to measure the amount of oxygen (O_2) evolved [42,48,49].

4. Nanoarchitectonics of Layered TMCs

4.1. Single-Layered Ternary TMCs

The layered ternary TMCs have a great deal of promise in overwhelming the constraints associated with binary TMCs such as MoS_2 in H_2 production. To evidence, the performance of the ternary TMCs, Tiwari et al. demonstrated highly stable layered TMCs, which consist of Mo and Cu (two transition metals) sandwiched with S (one chalcogen) (i.e., Cu_2MoS_4) through the facile solution-processing approach. Furthermore, the results also demonstrated a novel approach to exfoliating the layers of the developed materials (Cu_2MoS_4) by means of anionic doping of larger-sized Se. The representation of the exfoliated ternary TMCs is provided in Figure 2a [50]. Generally, in TMCs, the transition metal ions reduce the ΔGH of H_{ads} on the edge site of chalcogen atoms and tend to boost their catalytic performance. For the adsorption of hydrogen in the instance of Cu_2MoS_4 , there are three different types of edge sites: Cu, Mo, and S. Most of the catalytically active sites are Mo-edges, which are partially covered by sulfur atoms absorbed. Incorporating Cu ions causes the sulfur (S) edges to likewise become catalytically active. In this case, Se ions (negatively charged; -2) take the place of part of the S ions (negatively charged; -2) in Cu_2MoS_4 to become $\text{Cu}_2\text{Mo}(\text{S}_y\text{Se}_{1-y})_4$. The Mo-binding Se-edges become catalytically active when the Se ions are present at the S-edges. As a result, the single-layered ternary TMC achieved by controlled doping of Se ($\text{Cu}_2\text{Mo}(\text{S}_y\text{Se}_{1-y})_4$) resulted in the enhanced electrocatalytic activity of HER. The single-layered ternary TMCs exhibit robust electrocatalytic (HER) activity with an onset potential of 96 mV with the corresponding Tafel slope of 52 mV/dec compared with other multilayered ternary TMCs. Since there are more active sites in single-layered Se-doped materials than in multilayered samples, they are more effective against HER. This is further supported by the fact that single-layered TMCs have 68 times more electrochemical active area than bulk (multilayered) samples. Further evidence that the higher Se atom doping is not as effective for HER due to the inhibition of the active S vacancy, which is responsible for HER's hydrodesulfurization, comes from the fact that multilayered samples had a 23 times lower electrochemical active area than single-layered TMC. Moreover, the developed single-layered ternary TMCs were reported to be highly stable in electrolysis even after 1000 cycles for 15 h in acidic electrolytic conditions, suggesting a new method for the real-time applications of TMCs in H_2 production [21,36,50,51].

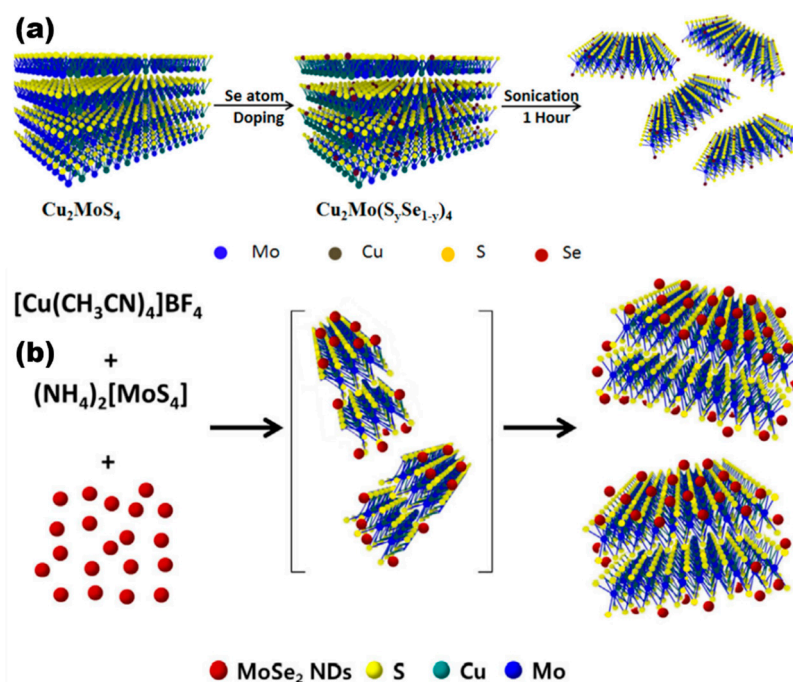


Figure 2. Schematic representation of Cu_2MoS_4 (a) single layered, and (b) nanodots [50,52]. Reproduced with permission from Tiwari et al., Nano Energy, Elsevier, 2016 and Kim et al., Chempluschem, Wiley, 2017.

4.2. Nanodots

Similarly, the ternary TMCs composed of Cu and Mo-based (Cu_2MoS_4) nanosheets demonstrated by Kim et al. evidence the enhanced electrocatalytic hydrogen generation. The experiment hypothesizes the decoration of molybdenum selenide (MoSe_2) nanodots (NDs) over the basal planes of few-layered Cu_2MoS_4 nanosheets through an in situ solution processing approach for the electrocatalytic HER activity in water splitting. The interaction of the chalcogen atoms in the ternary TMCs and the transition metals in the NDs induces high catalytically active sites. As in the developed ternary TMCs, the layers are connected by the van der Waals interactions between covalently bonded transition metal atoms and chalcogen atoms (Figure 2b) [52]. The active hydrodesulfurization catalyst in Cu_2MoS_4 is due to sulfur vacancies in the edge sites, whereas the basal planes are inactive due to less exposed transition metals and fewer vacancies of S-atom [53]. Additionally, the Se and S atoms have similar electronegativity and tend to have strong enough interaction of NDs and ternary TMCs to help in addressing the stability problem during the electrolysis procedures [54,55]. It also suggested that the most effective way to increase the catalytic activity of Cu_2MoS_4 is to use NDs with a controlled size, which can be regulated during the synthesis of ND-decorated nanosheets. For instance, the 20 mL of MoSe_2 NDs in ternary TMCs synthesis exhibit the lowest onset potential of 157 mV at a current density of 10 mA/cm^2 , with a corresponding Tafel slope of 72.6 mV/dec . Further, the NDs decorated ternary TMCs exhibit extremely stable conditions in an acidic medium during the continuous electrolysis process [52].

4.3. Nanocrystals

Multinary metal chalcogenides nanocrystals possess the strong potential to replace classic nanodot-structured TMCs in several applications, including water splitting. The nanocrystals offer a unique characteristic of the photo-physical (UV and visible range) and electrochemical properties [56]. The crystalline structure and fundamental electronic properties of the nanocrystal-structured ternary TMCs provide ease of dopant ion accommodation in the lattice with tunable bandgap energy [57].

4.4. Nanotubes

The one-dimensional (1D) TMC nanostructure is anticipated to provide 1D electron transfer channels, facilitating the electrolyte penetration and increase in the amount of reaction area; however, investigation on 1D ternary TMCs for water splitting has been scarce until now. One of the often-described approaches to manufacturing nanomaterials with varied morphologies, advantageous crystal facets, and regulated sizes and thicknesses by adjusting experimental parameters such as temperature, solvent, time, etc. is the hydrothermal/solvothermal technique. The synthesis procedure is referred to as the hydrothermal method if water is employed as the solvent, whereas the solvothermal method uses organic solvents. In closed steel containers, referred to as “autoclaves”, a heterogeneous reaction takes place in the presence of an aqueous solvent or mineralizers at high pressure and low temperature in order to dissolve and recrystallize the materials that are relatively intractable under normal circumstances [58–60]. For instance, the solvothermal synthesis of $\text{MoS}_{2-x}\text{Se}_{2(1-x)}$ nanotubes for the enhanced electrocatalytic HER activity in water splitting was carried out by tuning the chemical (chalcogens) composition, which results in the expansion of interlayer spacing of the ternary TMCs [61]. The SEM images of the synthesized ternary $\text{MoS}_{2-x}\text{Se}_{2(1-x)}$ nanotubes are shown in Figure 3. Figure 3a displays the morphology of the MoS_2 with an increase in the length of nanotubes ($\sim 3\text{--}4\text{ }\mu\text{m}$), and, upon thermal post-treatment of the sample for the form of $\text{MoS}_{2-x}\text{Se}_{2(1-x)}$, results in drastic compression in the length of the nanotubes. Specifically, the selenization at higher temperatures and for longer periods results in substantially rough surfaces of the $\text{MoS}_{2-x}\text{Se}_{2(1-x)}$ nanotubes, which validates the hollow interiors and hierarchical architectures after being selenized at $800\text{ }^\circ\text{C}$ for 1 h (Figure 3b,c). Furthermore, the expansion of interlayer spacing with the hierarchical assembled nanotubes of ternary TMCs benefits the hydrogen adsorption energy during the electrocatalytic activity in water splitting [61,62].

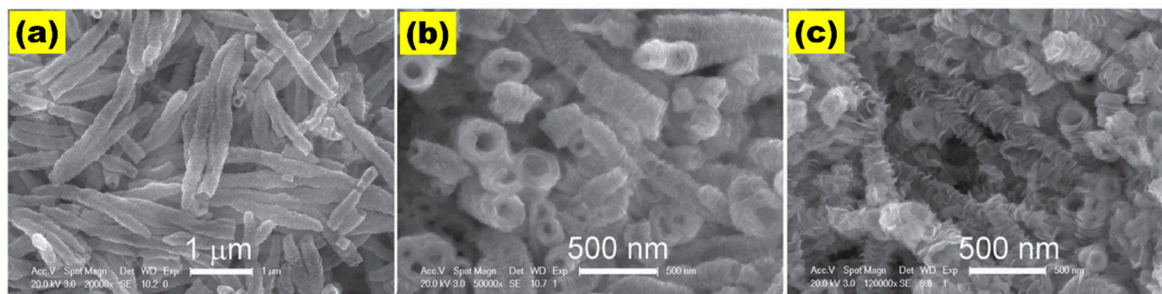


Figure 3. SEM images of nanotubes (a) MoS_2 , and (b,c) $\text{MoS}_{2-x}\text{Se}_{2(1-x)}$ [61]. Reproduced with permission from Zhang et al., Small, Wiley, 2016.

4.5. Nanowires

Similarly, the 1D nanowires (NWs) and their composites based on NWs have recently been demonstrated to offer a technique for customizing the density of states surrounding the Fermi level, with decreased thermal conductivity, and with compatibility with flexible substrates [63–65]. The NWs offer the potential benefit of low-cost manufacture for large-scale applications in several fields of applications, including catalysis [66–69]. For instance, the ultrathin ternary metal/Te/Se NWs have been developed with tunable composition and high aspect ratios via a solution-based hot-injection approach. By using the mentioned approach, we are able to add a variety of different metal species while preserving single-phase ternary TMCs with well-defined crystal and nanowire structures by using $\text{Te}_{1-x}\text{Se}_x$ templates, where the chemical reactivity between the Te and Se atoms will be balanced. The synthetic method entails three steps: (1) the synthesis of ultrathin Te nanowires as a precursor, (2) the Te nanowires are applied to create $\text{Te}_x\text{Se}_{1-x}$ nanowires with the adjustable aspect ratios, and (3) the transformation of the $\text{Te}_x\text{Se}_{1-x}$ nanowires into a series of ternary metal- $\text{Te}_x\text{Se}_{1-x}$ nanowires by the hot-injection of suitable metal precursors ($\text{Bi}_2(\text{Te}_x\text{Se}_{1-x})_3$, $\text{Ag}_2\text{Te}_x\text{Se}_{1-x}$, $\text{Cu}_{1.75}\text{Te}_x\text{Se}_{1-x}$, $\text{CdTe}_x\text{Se}_{1-x}$, and $\text{PbTe}_x\text{Se}_{1-x}$) under particular circumstances.

The schematic representation of NWs synthesis is provided in Figure 4a [68]. The rapid inclusion of metal atoms into the Te/Se NWs throughout the synthesis phase is the main reaction in the transformation. The reaction time may vary depending on the metal precursors; however, all the reactions taking place within 3 h are very stable and are able to successfully synthesize composition-adjusted metal/Te/Se ternary NWs [70]. The demonstrated work on ternary ultrathin nanowire-structured TMCs opens the path for the scalable synthesis of the ternary TMCs [68].

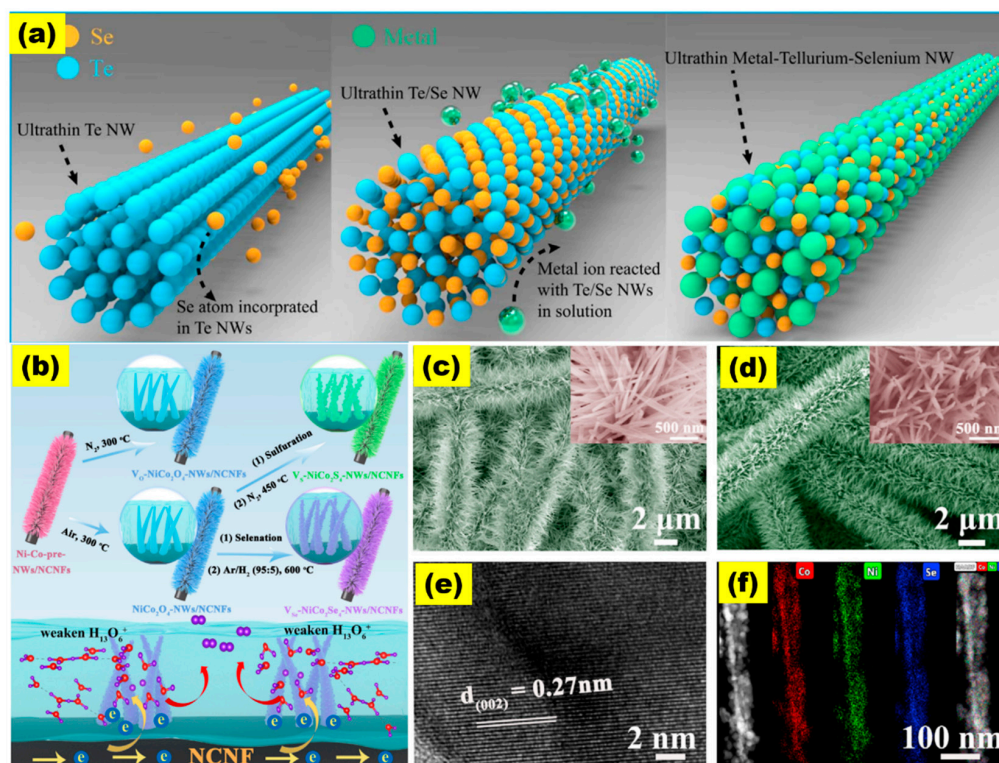


Figure 4. The ternary TMCs: schematic representation of (a) nanowires, (b) nanofibers, and (c–f) morphology and mapping of NiCo_2Se_4 [68,71]. Reproduced with permission from Zhou et al., Nano Energy, Elsevier, 2016 and Zong et al., Electrochim Acta, Elsevier, 2020.

4.6. Nanofibers

The fibrous structures of the ternary TMCs offer similar kind of characteristics to nanowires, which include rapid electronic transport, high active catalytic surfaces, and so on. Considering this fact, Zong et al. fabricated various nanofiber-structured nickel cobalt-based ternary TMCs comprised of NiCo_2A_4 ($\text{A}=\text{S}$ and Se) by creating an anion vacancy. The scheme (Figure 4b) illustrates various ternary TMCs for the hydrogen production process in water splitting, and Figure 4c–f represent the obtained morphology [71]. The typical synthesis process involves the intrinsically high volatile sulfur and selenium-rich vacancy for NiCo_2S_4 and NiCo_2Se_4 , respectively, by the anionic substitution and thermal treatment [72]. The developed ternary TMC architecture with the nanofiber templates induces the formation of anchoring nanowired TMCs over the direction-oriented growth on nanofibers. Both (NiCo_2S_4 and NiCo_2Se_4) the ternary TMCs offer the benefits of an enhanced number of active sites possessing large surface areas for electrochemical water splitting. The NiCo_2Se_4 nanofibers, which are rich in selenium vacancies, exhibit stronger electrocatalytic activity than the other chalcogens (NiCo_2S_4), with a Tafel slope of 49.8 mV/dec^{-1} and a low overpotential of 168 mV at 10 mA/cm^2 , attributing to its anionic vacancy size [71,72].

4.7. Nanospheres and Nanospheroids

Benefiting from the hollow and sphere-structured TMCs in water-splitting reactions, a controllable synthesis of nickel sulfoselenide ($\text{NiS}_{2(1-x)}\text{Se}_{2x}$) electrocatalyst via the hydrothermal method was reported by Zeng et al. [73]. The schematic representation for the formation of ternary TMCs ($\text{NiS}_{2(1-x)}\text{Se}_{2x}$) is provided in Figure 5a–c. The enhanced electrocatalytic activity of the ternary TMCs was achieved by regulating the degree of S/Se in $\text{NiS}_{2(1-x)}\text{Se}_{2x}$ to boost its intrinsic activity by changing its electronic structure. The TMCs with a particular chemical composition of $\text{Ni}(\text{S}_{0.5}\text{Se}_{0.5})_2$ exhibit significant bifunctional electrocatalytic activity (OER and HER) in a neutral medium, taking use of their distinctive structural characteristics and the anion doping effect.

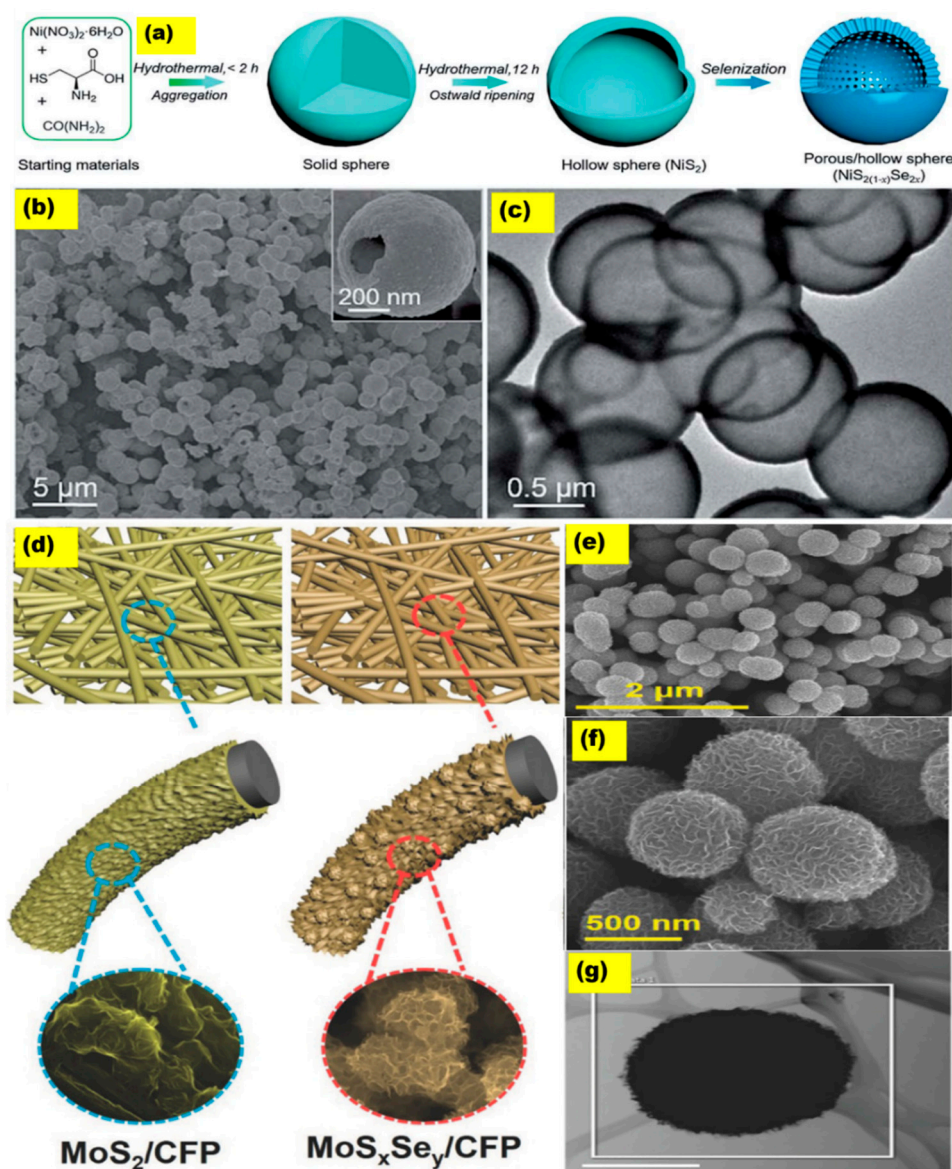


Figure 5. (a–c) Nanosphered ternary $\text{NiS}_{2(1-x)}\text{Se}_{2x}$, and (d–g) Nanospheroid MoS_xSe_y [73,74]. Reproduced with permission from Zeng et al., J Mater Chem A, Royal Society of Chemistry (RSC), 2019 and Bose et al., Small, Wiley, 2018.

This research shows the potential for creating a novel kind of abundant electrocatalyst that is attractive and useful for neutral-pH water electrolysis. Furthermore, it also provides perspectives on creating advanced electrocatalysts and an elegant strategy for enhancing the efficiency of electrochemical catalysis [73].

Bose et al. demonstrated the fabrication of nanospheroid-structured ternary molybdenum sulphoselenide (MoS_xSe_y) on carbon filter paper using appropriate precursors (Mo, S, and Se) by the hydrothermal approach. A typical hydrothermal approach involves the reaction of different sources of precursor and reagents such as molybdic acid (for Mo), thioacetamide (for S), and selenium dioxide (for Se) at a retained temperature of 180 °C for 24 h. Further, the experiments report the electrocatalytic activity of the different binary, ternary, and quaternary TMCs for H_2 production. From the taken reactants, the theoretical growth and reaction mechanism is illustrated in Figure 5d–g. The results display good electrocatalytic activity of the ternary TMCs with the composition of $\text{Mo}_{37.3}\text{S}_{46.9}\text{Se}_{15.8}$ ascribed to its nanoarchitectonic (nanospheroids) structure with a synergistic effect of the large exposed active sites and intrinsic activity [74].

4.8. MOF Nanoarchitectures

The metal–organic framework (MOF) nanoarchitectures with extremely high surface areas, tunable nanostructures, and excellent porosities have made significant strides in engineering research and are now being considered as potential raw materials for the creation of highly effective electrochemical water-splitting catalysts. The creation of catalytic centers for electrocatalysts produced from MOF-based materials, as well as optimization and structural functionalization at the atomic and molecular levels, contribute to the rapidly expanding advances in active catalytic activities and fundamental processes. MOFs can be viewed as essential materials to introduce active guest species, such as metal complexes, nanoparticles, and polyoxometalates (POMs), through covalent or noncovalent bonds (electrostatic, π – π , and host–guest interactions), and support the formation of their well-defined pore structures by using a variety of organic linkers. In many instances, the catalytic activity could be enhanced by the synergistic interaction between the guests and MOFs [75]. Due to its inherent benefits, including quick mass and electron transfer, adjustable architectures, and more exposed active sites, 2D MOFs have also been shown to be potential electrocatalytic materials in various studies [76,77]. Greater exposure of the active surface sites might possibly be made possible by converting bulk MOF crystals into 2D nanosheets. Through a simple method of one-step chemical bath deposition, Duan et al. created ultrathin nanosheet arrays of 2D MOFs on a variety of substrates, demonstrating improved performance for the OER, HER, and overall water splitting. For instance, using a straightforward sonication-assisted solution technique, novel 2D Co-BDC/ MoS_2 hybrid nanosheets were developed and created as effective electrocatalysts for alkaline HER. In the Co-BDC/ MoS_2 system (BDC stands for 1,4-benzenedicarboxylate, $\text{C}_8\text{H}_4\text{O}_4$), the addition of Co-BDC caused a partial phase transfer from 2H- MoS_2 to 1T- MoS_2 , which greatly increases HER activity. More crucially, the alkaline HER would benefit greatly from a well-designed Co-BDC/ MoS_2 interface. The alkaline HER's rate-determining water dissociation step is made easier by Co-BDC, while the subsequent H_2 -generation step benefits from modified MoS_2 [78]. Due to kinetic restrictions and its critical significance for future energy harvesting, it is still difficult to demonstrate a highly effective non-noble bifunctional catalyst for complete water electrolysis. A simple hydrothermal approach was used to create a low-cost, integrated composite comprising a NiCo metal and organic framework that was then carbonized and phosphorized for the electrochemical oxygen and hydrogen evolution reactions. It had a lower overpotential of 184 mV for the oxygen evolution reaction (OER) and 84 mV for the HER in 1.0 M KOH and 0.5 M H_2SO_4 electrolytes to reach a current density of 10 mA/cm^2 , with a slight Tafel slope of 63 mV dec^{-1} for the OER and 96 mV dec^{-1} for the HER, exhibiting exceptional performance. The research outcomes are significantly superior to those of the benchmark catalyst used in the industry [79].

Likewise, there are several nanoarchitectured TMCs that have been developed and reported for water-splitting applications. Despite the different nanostructures reported, the synthesis approach also plays an important role in determining the catalytic performance of water splitting. Thus, the advantages/disadvantages of various synthesis approaches are comparatively provided in Table 1.

Table 1. Advantages/Disadvantages of various synthesis approaches for TMCs.

Synthesis Approaches	Advantages/Disadvantages	Ref
Hydrothermal/Solvothermal Method	Produces nanomaterials with various morphologies and thicknesses at high pressure and low temperature; can synthesize high-quality large crystals; cost of equipment is high	[61,80]
Microwave-assisted Synthesis	Requires less time/rapid process; size can be controlled	[81,82]
Electrodeposition Method	Rapid and single-step process; used to produce homogeneous and high-purity crystalline materials at the cathode of the electrochemical system during the coating process	[83]
Sulfidation and Selenization	Solution-phase conversion; facile and selectable synthesis method	[73]
Chemical Vapor Deposition (CVD) Method	Gas-phase aerosol process for producing high-purity nanoparticles; mainly used for large-scale thin-film production	[84]
Photoreduction	Requires higher photon energy; can synthesize materials with large surface area and many active sites	[85]
Refluxing Method	Large-scale synthesis method; facile and cost-effective	[86]
Sputtering	0D, 1D, and 2D materials can be prepared; used for depositing materials with high melting point; as electrons can be focalized, it is possible to obtain very localized heating on the material to evaporate with a high density of evaporation power	[87,88]

5. Layered Ternary TMCs as Bifunctional Electrocatalysts in Water Splitting

The electron-rich structure of the layered TMCs exhibits relatively low inherent electrical resistivity and quick charge carrier movement during OER and HER processes. Additionally, the TMCs could maintain chemical stability in hostile settings (strong acids or alkalis). As a result, they have recently attracted a lot of interest due to their ability to fully split the water molecules in a variety of electrolytes with varying pH levels [20,73,82,89–91]. Tao et al. developed nanoclustered nickel cobaltite telluride (NiCo_2Te_4) by the surface modification approach for the bifunctional electrocatalysts in overall water splitting at neutral conditions. As a straightforward approach, surface modification (using surface ligands) can dramatically boost the catalytic activity toward an efficient hydrogen and oxygen evolution reaction at the same time. By utilizing this newly created nanocluster ternary TMC electrocatalyst, a bifunctional (two-electrode)-based water electrolysis cell operating at a low bias voltage of 1.55 V at a current density of 10 mA/cm^2 with exceptional stability for 30 h in a solution with a pH near neutral has been demonstrated [92]. The hydrogen adsorption-free energy (ΔG_{H}) of the TMC electrocatalysts is shown in Figure 6a. Due to its weak 2D planar π -conjugation structure and anhydride terminal groups ($\text{O}=\text{C}-\text{O}-\text{C}=\text{O}$), the surface ligand has a higher ΔG_{H} value (~ 6.5 eV) than others. The electronegativity of the ternary electrocatalyst decreases, and the ΔG_{H} between the NiCo_2Te_4 and ligands are both reduced by a strong ionic connection (O-Te) between the TMCs and the surface ligand. As a result, the NiCo_2Te_4 surface may release atomic hydrogen with ease, thereby boosting the catalytic activities during the water-splitting process [93]. Furthermore, the DFT simulations suggest that the surface ligand changed the NiCo_2Te_4 electrons' energy distributions towards the favored catalytic processes [92]. Likewise, the doping of metals (Co) in the binary TMCs to form the ternary Co-MoS₂ nanosheets supports achieving higher conductivity and lower hydrogen adsorption energy toward HER and produces more OER catalytic active centers [94]. In both acidic and alkaline conditions, the ternary TMCs (Co-MoS₂) exhibited the best HER activity, comparable to that of Pt/C, suggesting that an appropriate Co doping quantity is crucial for the successful regulation of the electronic

structure [95,96]. The onset potentials and overpotentials of Co-MoS₂ were specifically 0.04/0.03 V (vs. RHE) and 60/90 mV in 0.5 M H₂SO₄ and 1.0 M KOH, respectively, at 10 mA/cm². The reported results are consistent with the fact that the HER activity in the acidic media is higher than in the alkaline media [96,97]. Likewise, with onset potentials of 1.68/1.33 V (vs. RHE) in 0.5 M H₂SO₄ and 1.0 M KOH, and overpotentials of 540/190 mV at 10 mA cm², it has the highest OER activity in both acidic and alkaline conditions. Its excellent water-splitting durability is demonstrated at a constant voltage of 1.58 V in 1.0 M KOH, validating the viability of ternary Co-MoS₂ TMCs as a bifunctional electrocatalyst in both acidic and alkaline conditions [94]. Following this work, a series of NiS_{2(1-x)}Se_{2x} hollow/porous spheres (x = 0, 0.25, 0.5, and 0.72) made through the hydrothermal process and the degree of the selenization tends to attain the satisfactory and the ideal bifunctional (OER and HER) behavior of η_{10} overpotential of 501 and 124 mV of ternary electrocatalysts. The composition of Ni(S_{0.5}Se_{0.5})₂ in 1M phosphate-buffered saline solution was attributable to the anion Se doping's optimal electronic state as well as its special structural characteristics (Figure 6b). Then, using the Ni(S_{0.5}Se_{0.5})₂ as a bifunctional electrode (anode and cathode), it was possible to create an overall water splitting that could deliver a lower cell voltage of 1.87 V at 10 mA/cm² in neutral conditions (Figure 6b) [73].

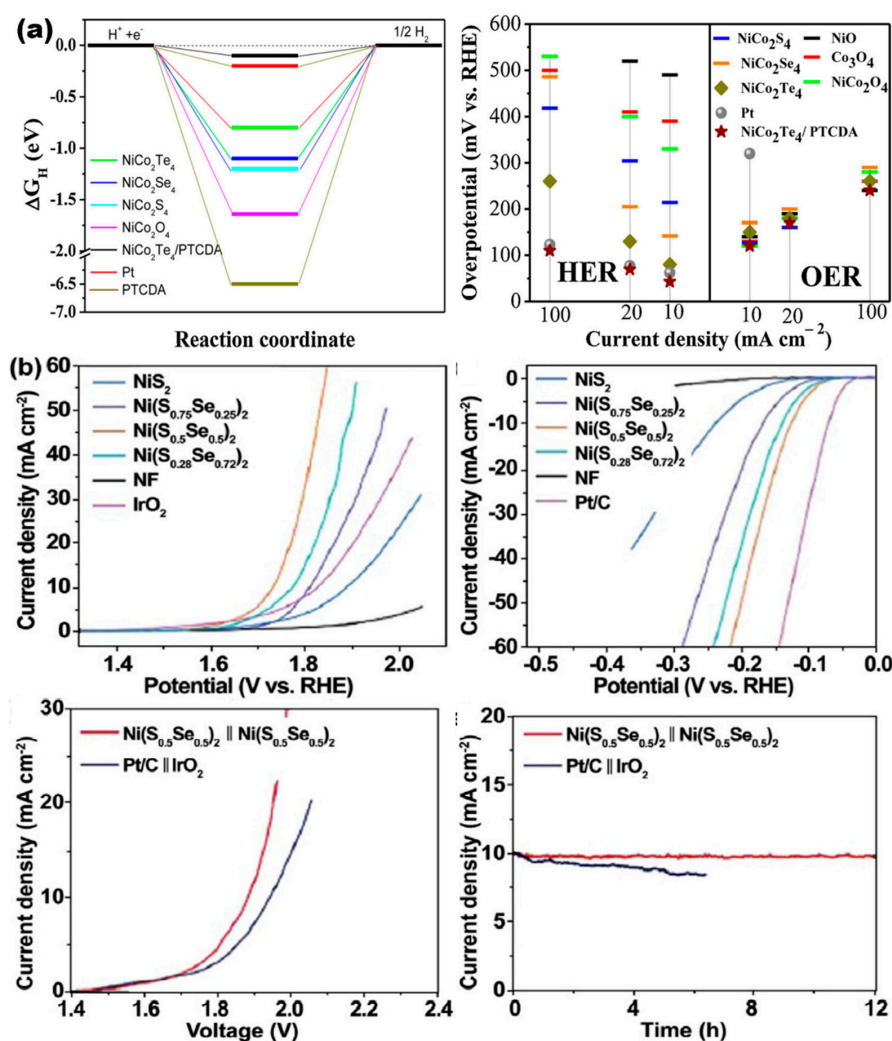


Figure 6. (a) NiCo₂S₄, NiCo₂Se₄, NiCo₂Te₄ hydrogen adsorption free energy (ΔG_H) diagrams and their catalysts performance, and NiS_{2(1-x)}Se_{2x}, and (b) OER, HER polarization curves, overall water-splitting activities and the corresponding time–current density [73,92]. Reproduced with permission from Zeng et al., J Mater Chem A, Royal Society of Chemistry (RSC), 2019 and Tao et al., Appl Catal B Environ., Elsevier, 2019.

It has also been investigated to greatly increase the electrocatalytic OER and HER activity of undoped pentlandite-type cobalt sulfide (Co_9S_8), designated as $\text{Co}_9\text{S}_4\text{P}_4$, under neutral circumstances. Imparting phosphor in the Co_9S_8 is beneficial to boosting the electrical conductivity, surface area, and charge transfer for water-splitting reactions. In contrast to the benchmark material, Pt/C- IrO_2 (1.72 V), $\text{Co}_9\text{S}_4\text{P}_4$ material demonstrated an applied voltage of just about 1.67 V to obtain 10 mA/cm^2 , as well as a negligible change in applied voltage following a continuous 24 h galvanostatic electrolysis at 10 mA/cm^2 in a neutral electrolyzer [98].

6. Tactics for Enhancing Electrocatalytic Activity

The nanoarchitectonics layered ternary TMCs have garnered interest as one of the most promising electrocatalysts for water splitting due to their distinctive structure. The basal plane of TMCs is catalytically inert; however, the novel findings indicate that the stacked TMC edge sites are active for electrocatalytic activity because these edge sites possess a nearly optimum hydrogen adsorption-free energy for water splitting [22,32,99]. There are three main ways to improve the electrocatalytic characteristics of layered TMCs: (i) edge engineering for boosting the active sites, (ii) activating the basal planes by altering their chemical composition, and (iii) strain regulation through the structural and chemical changes.

6.1. Edge Engineered Layered TMCs

The optimization of the basal plane-to-edge ratio creates a new opportunity for improving catalyst performance, which has been made possible by the observation of multilayered TMCs edge activity (for electrocatalytic activity). The density of the accessible edges at the surface of TMCs has been improved in recent years in several ways, including vertical alignment, porous structure, stepped surface structure, hollow structure (HS), and three-dimensional nanopatterning, nanoarchitectonics [100–102]. The creation of MoO_3 and MoS_2 core-shell nanowires with a vertical orientation is one such method for achieving this goal, with the use of this technique exhibiting effective electrocatalytic activity for separating water molecules (H_2 and O_2) in an acidic medium by exposing the high surface electrodes with significant amounts of edge-exposed MoS_2 [102]. Additionally, Cui et al. reported MoS_2 and MoSe_2 thin films with vertically aligned layers developed on flat Mo substrates to increase the exposure of edges. The edge-terminated TMCs demonstrate effective electrocatalytic activity for water splitting (Figure 7a) [23]. Similarly, Wang et al. created MoSe_2 and WSe_2 on curved nanowires that were vertically orientated. The surface area for effective electrocatalytic activity is increased while the exposed edge sites are maximized in these reported structures [24]. By stretching or compressing the molecular layers, altering the electronic structures of transition metal dichalcogenides, and resulting in an even greater improvement in the electrocatalytic activities of metal dichalcogenides, the formation of vertical structures of TMCs on the curved surfaces may result in strain. To boost the electrocatalytic activity, Kibsgaard et al. constructed MoS_2 with a double-gyroid (DG) shape that preferentially exposes the active edge sites (Figure 7b,c) [103]. In the fabricated contiguous large-area thin films of a highly ordered double-gyroid MoS_2 bi-continuous network, a considerable portion of the edge sites have a high surface area and effectively split water through electrocatalysis. Theoretically, stepped-edge customized MoS_2 has been demonstrated to be a more effective technique to increase the catalytic activity than the flat edge site MoS_2 . Figure 7d,e show the vertical arrays of stepped-edge, surface-terminated MoS_2 nanosheets studied by Hu et al. shown to be an excellent and very stable electrocatalyst for water splitting when compared to the flat-edge surface-terminated MoS_2 [104]. For effective electrocatalytic activity, the single-crystal MoS_2 nanobelts completely covered in edge sites on the top surface have also been described. These parallel-stacked atomic layers on the MoS_2 basal planes of these nanobelt structures maximize the exposure of active edge sites for efficient electrocatalytic activity for water splitting [105]. In a similar way, to create highly electrocatalytic MoSe_2 films, Saadi et al. reported using an operando

synthesis approach [106]. This method exposes more edge sites and offers a large surface area for effective electrocatalytic activity. Additionally, the effective electrocatalytic activity for water-splitting has been reported to be obtained using flexible electrodes containing edge-oriented MoS₂ [107]. The electrochemical anodization of molybdenum metal, followed by interaction with sulfur vapor, produces the edge-oriented flexible film of MoS₂. The most electrocatalytic activity of TMCs can be utilized by combining a high surface area with a high percentage of exposed edge sites and tailored electronic architectures. A multiscale structural and electrical control of MoS₂ foam as an electrocatalyst for water splitting was reported by Deng et al. [96]. To fine-tune the electronic structure of MoS₂, which improves the electrocatalytic activity of the edges of MoS₂, the three-dimensional, vertically aligned MoS₂-foam is doped with Co atoms (Figure 7f,g). The commercial nickel (Ni) foam supports boosting the electrocatalytic activity of the TMCs by acting as a template; moreover, such a simple approach finds a way in a scalable method to expose the maximum edge-oriented TMCs. In this instance, the vertically aligned arrays of the MoS₂ nanosheets over Ni foam exhibit the enhanced H₂ production activity that may be applied in practice by maximizing exposure of atomistic-level MoS₂ edge sites [105,106]. Even though the structural engineering of TMCs has demonstrated higher electrocatalytic activity, it has been anticipated that even better performance can be attained if the 3-dimensional (3D) template's effective feature size is reduced to the order of nanoscale [108]. Following this strategy, an extremely stable and active electrocatalyst has been created for the massive production of H₂ using the 3D nanopatterning approach. Based on the existing technology, the TMCs were continuously nanopatterned (3D) using proximity-field nanopatterning (PnP) and electrode placement, then a solvent-assisted hydrothermal process. The electrocatalytic activity of such fabricated 3D nanopatterned TMCs was higher than that of TMCs grown on Ni foam with a low loading of active material for water splitting (Figure 7h,e,k) [17,106,108].

6.2. Doping/Vacancy in Layered TMCs

Despite considerable advancements in edge engineering, the layered TMCs are still limited in their electrode activities, since only the edge sites are responsible for the positive electrode activity. Generally, the chemical absorption at the active sites of the TMCs can be improvised by the polarizing effect in orbit coupling, which tailors the electron density. In this regard, to improve the electrochemical performance of layered TMCs and increase the number of active sites for electrocatalytic activity, the introduction of heteroatoms or vacancies is suggested as one of the successful techniques [109,110]. The heteroatom introduction might enhance the reactive species' adsorption energies during the water-splitting mechanism. It is possible to create a bifunctional catalyst by increasing the active sites, controlling electronic structure, and creating defects and distortions in the lattice [94,111–113]. For example, the covalent doping approach of cobalt (Co) into MoS₂ aids induces the bifunctional property of the ternary electrocatalysts in the water-splitting reactions (OER and HER). By optimizing the catalysts' electronic structure (covalently doped Co into MoS₂), the ΔGH^* could be decreased with an increase in intrinsic conductivity, leading toward the improved performance of HER. The production of high-valence-state Co species in an alkaline solution under anodic potentials is attributed to the increase in OER activity. The developed ideal ternary TMCs displayed the functions of both OER and HER with overpotentials of 260 and 48 mV at 10 mA/cm², respectively. Similarly, the developed ternary TMCs (by covalent doping) achieved nearly 100% Faradaic efficiency in an alkaline medium producing 4.5 and 9.1 $\mu\text{mol min}^{-1}$ of O₂ and H₂, respectively [114,115]. In a similar way, the copper clusters incorporated into cobalt sulfide and deposited over copper foam (Cu@CoS_x/CF) result in serving bifunctional ternary electrocatalysts towards water splitting in an alkaline medium, thereby yielding a current density of 10 mA cm² at 1.5 V. Additionally, the Cu@CoS_x/CF electrolyzer could maintain the current density of 100 mA cm² over 200 h of the water catalytic reaction at 1.8 V without obvious current reduction. According to the experimental and theoretical findings, the ternary Cu@CoS_x/CF had good catalytic performance due to the synergistic interactions between Cu and CoS_x.

Furthermore, the water molecules adsorption and electronic transport on the catalytic surface can be sped up by facilitating the interfacial charge redistribution of Cu@CoS_x. Additionally, the water-splitting reaction kinetics were also made easier by the fact that favored the dissociation of water [116].

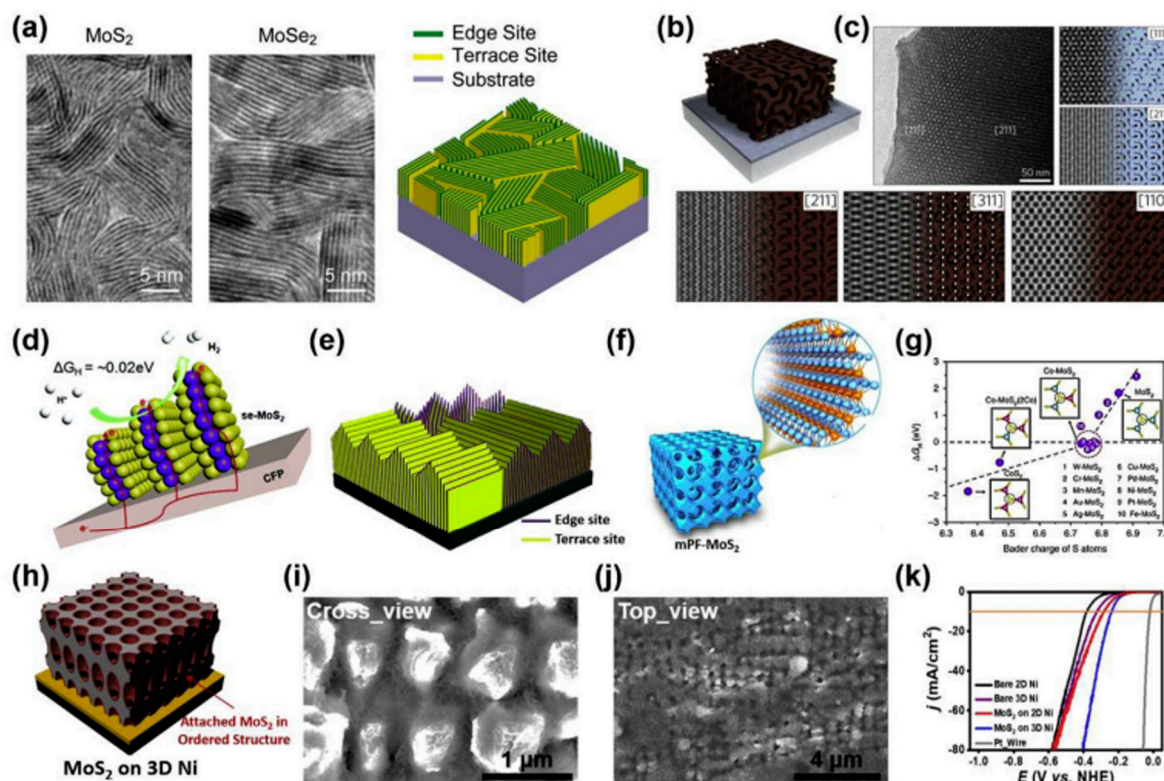


Figure 7. (a) Edge-terminated MoS₂ films with layers and the corresponding high-resolution transmission electron microscopy (HRTEM) images, schematic illustration (b,c) for double-gyroid mesoporous MoS₂ and the corresponding HRTEM images, (d,e) vertically aligned stepped-edge surface-terminated MoS₂ nanosheet arrays and the corresponding DGH*, (f,g) DGH* for Co doped mesoporous MoS₂, and (h–k) MoS₂ with 3D nanopatterns on Ni with its SEM and electrocatalytic results [17,23,96,103,104]. Reproduced with permission from Kim et al., Int J Hydrogen Energy, Elsevier, 2019; Kong et al., Nano Lett., American Chemical Society (ACS), 2013; Deng et al., Nat Commun, Nature, 2017; Kibsgaard et al., Nat Mater, Nature, 2013; and Hu et al., Energy Environ Sci., Royal Society of Chemistry (RSC), 2017.

6.3. Strain Regulation in Layered TMCs

The electronic structure of the ternary TMCs can be customized by altering the atomic configuration of the electrocatalyst through lattice or chemical strain. There are numerous techniques, including doping, vacancy creation, core–shell structuring, and lattice mismatch, that have been demonstrated to create the inherent strain in TMCs [117–120]. The electrocatalytic activity of TMCs is improved by the easy induction of inherent strain by the core–shell structure, which enables an upshift in the d-band center. By tuning the stacking of MoS₂ shell layers, Zhu et al. reported a controllable and accurate tensile strain for effective electrocatalytic activity in a Co₉S₈/MoS₂ core–shell structure (Figure 8a,b) [117]. The stabilization of the intermediate HER for capturing and release of H₂ ions can be achieved with the regulated charge transfer in heteroepitaxial lattice strain in the core–shell structure, hydrogen atom absorption (DEH), and the transition-state (DE2H) energy barriers, respectively. Similarly, a Mo₂C/MoS₂ core–shell configuration was reported by Tiwari et al. (Figure 8c) [118]; in order to activate the electrocatalytic activity, molecular spin-coupled core (Mo₂C) MoS₂ was created. The MoS₂'s curved shells provide the lattice strain, which

enhances the kinetics of electrocatalysis, and spin coupling ensures rapid ion diffusion. Additionally, lattice mismatch in the core-shell-structured TMCs induced the intrinsic strain for the enhanced electrocatalytic activity in water splitting [121]. Likewise, the MoS₂ electrocatalytic activity was enhanced by creating intrinsic strain in the material through a lattice mismatch with the Au substrate (Figure 8d,e). It is demonstrated that the improved electrocatalytic activity of MoS₂ is due to out-of-plane lattice strain, which controls the charge density distribution and atom migration while lowering the band gap and DGH* [119,122].

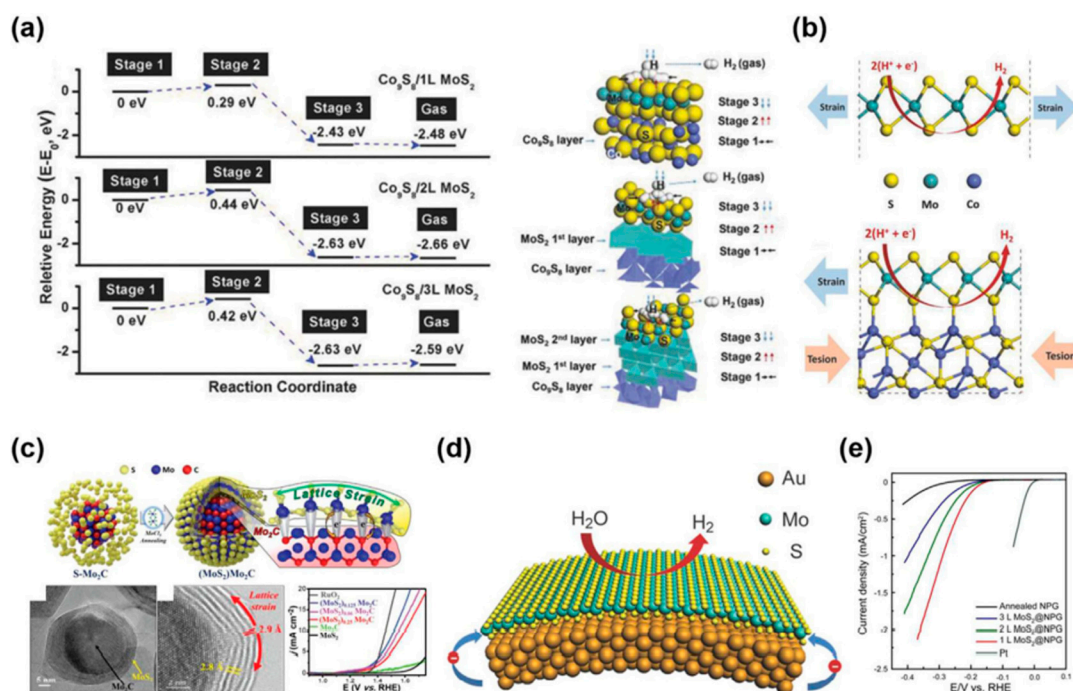


Figure 8. core-shell-structured (a) Co₉S₈/MoS₂'s reaction pathways of H₂ atom/molecule adsorption/desorption; (b) chemical models of the strained MoS₂, and Co₉S₈/MoS₂, schematic illustration for (c) the synthesis of Mo₂C/MoS₂ and corresponding TEM images and OER activity; (d) HER catalyzed; and (e) electrocatalytic performances by the monolayer MoS₂ at nanoporous metal [117–119]. Reproduced with permissions from Zhu et al., Adv Mater, Wiley, 2018; Tiwari et al., Adv Mater Interfaces, Wiley, 2019; and Tan et al., Adv Mater, Wiley, 2014.

6.4. Chemical Modification

Based on the prospective outcomes derived from the binary TMCs for the electrocatalyst, the ternary TMCs with a more complicated composition and structure can be presented through chemical modification. There are two ways to synthesize ternary TMCs from binary TMCs: (i) the doping or post-treatment approach, and (ii) the bottom-up synthesis approach. In the doping or post-treatment approach, the difference existing between the atomic radius of the doped and original atom causes the expansion or contrast in the lattice of the developed catalyst; moreover, it tends to change the bonding nature and electronic structure compared to the original system, which tends to induce the adsorption/desorption behavior in the reaction process. On the other hand, the bottom-up approach is considered one of the simplest ways to achieve the controlled morphology and growth of the ternary TMC-based electrocatalysts.

6.4.1. Double-Anion Ternary TMCs

Double-anion TMCs, which hold the ternary blends, were characterized by unique performance to activate the inner base plane of themselves. Because the non-metallic atoms have strong electronegativity, the introduction of non-metallic atoms can more effectively

change the electronic structure and chemical properties of the original materials, which provides support for improving the catalytic activity of the catalyst [123]. Xie et al. were the first to demonstrate the significant research activity of double-anion TMCs for HER. The oxygen concentration of MoS₂ flakes was regulated by adjusting the synthesis temperature, with higher oxygen contents being produced under lower temperature circumstances. With respect to the increased oxygen content, the flakes became more disordered until the complete amorphous formation. The best sample (2.28 at.% O and 35–40% disordered) displayed a Tafel slope of 55 mV/dec, which was significantly better than the result for pure MoS₂ (81 mV/dec). The results evidence the significance of double anion TMCs and the value of creating disorder or flaws in the basal plane [124]. The report made a research direction to focus on creating defects and/or oxidation of TMCs for boosting the electrocatalytic by activating its basal planes. Even though the proposed approach is successful in basal plane activation, there are some hurdles associated with the charge transporting activity (from electrocatalyst to electrode) causing a lowering of electrical conductivity owing to the O₂-rich or amorphous behavior of the TMCs. Hence, an alternative approach for the double-anion formation of TMCs can be achieved with S or Se doping or substitution. Xu et al. reported the doping of sulfur (S) in MoSe₂ by the simple hydrothermal approach tends to possess more catalytic reaction active sites, thereby boosting the electrocatalytic performance towards the H₂ production. Figure 9a,b present the HRTEM images of the S-doped MoSe₂ nanosheets with exposed edges and basal planes and a scheme demonstrating the unsaturated edges of nanodomains on the oriented basal plane (100) for proton adsorption with the corresponding polarization curves shown in Figure 9c [125]. Gong et al. [126] synthesized the ternary MoSSe electrocatalyst through the bottom-up approach by adjusting the ratio of S/Se in the MoCl₅ precursor for the HER activity. The study revealed a 93% retention of the current density over 8000 cycles with an overpotential of 164 mV at 10 mA/cm² and a Tafel slope of 48 mV/dec. In accordance with the earlier theoretical research on S and Se-based Mo systems, more negative H₂ adsorption will be exposed by selenide-based Mo edges ($\Delta GH = -140$ meV) on the other sulfide-based Mo edges possessing positive H₂ adsorption energy ($\Delta GH = 80$ meV) [127,128], suggesting the developed ternary TMCs (MoSSe) could reduce the adsorption energy value to nearly thermoneutral.

Telluride (Te) is another chalcogen that can be used to make effective electrocatalysts for water splitting, despite the fact that the two chalcogens (S and Se) have been investigated widely for electrocatalytic activity. Kosmala et al. fabricated the ternary MoSe_{2-x}Te_x films by molecular beam epitaxy and explored the materials for the electrocatalytic HER activity, and the results showed the overpotential of 410 mV and Tafel slope of 62 mV/dec at a current density of 10 mA/cm². The developed ternary TMC electrocatalyst exhibits abundant metallic twin boundaries and thermodynamically stable defects inducing the performance of the electrocatalytic activity in water splitting. It was also reported that pristine MoTe₂ exhibits more catalytic active sites than the pristine MoSe₂ fabricated under the same conditions, making a noteworthy optimal composition fabrication of Te-rich ternary TMCs (MoSe_{0.12}Te_{1.79}) [129]. However, the reported results are contradicted to the earlier conducted experimental and theoretical findings on the Te-based system [25,130], proposing Te cannot be intrinsically active catalysts in S or Se-based systems, thereby suggesting a new avenue to explore more investigations on the Te-based TMCs electrocatalysts.

It is anticipated that research in this area will continue to advance given the general availability of both dopant anions and synthesis techniques to produce double anion TMCs. However, it is important to note that reports published so far on double-anion TMCs has employed methods that are unable to create any kind of predictable ordering or arrangement of the replacing atoms. However, the periodic or ordered double anion structures, such as the Janus TMCs proposed by recent theoretical investigations, might produce unique electrocatalytic characteristics [128,131,132].

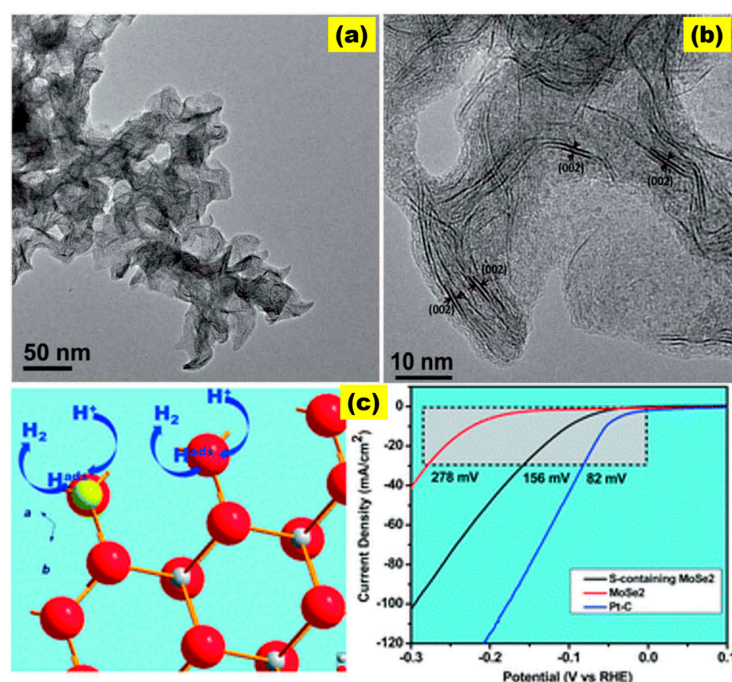


Figure 9. S-doped MoSe₂: (a,b) HRTEM images, and (c) the polarization curves [125]. Reproduced with permission from Xu et al., J Mater Chem A, Royal Society of Chemistry (RSC), 2014.

In these formations, the transition metal (Mo or W) has selenide on one side and sulfurization and the corresponding HER reaction on Janus TMCs is provided in Figure 10a [130]. However, the single-step synthesis method for these structures is difficult; they require a multi-step procedure that would restrict further investigation into their potential as electrocatalysts in water splitting [131]. Additionally, it has been forecasted that in the near future, the tactics exploiting the naturally high surface area beginning materials, such as Ni foam (shown in Figure 10b), would see an increase in popularity [67,133].

6.4.2. Double-Cation Ternary TMCs

Like double-anion TMCs, substantial research activity has been carried out on the double-cation TMC for electrocatalysts. The primary objectives in both (anion and cation) are to induce the typical basal plane to be active and produce additional active sites by defect or strain development. However, numerous investigations suggest that the electron density and local field is the primary advantage of double-cation TMCs because, for layered TMCs, there will not be a typical adsorption site in the transition metal atoms. Li et al. fabricated the Mo_{1-x}W_xS₂ by incorporating W into MoS₂ through the hydrothermal approach by varying the ratio of different metal precursors and investigating its cationic effect in the electrocatalytic activity of water splitting. Due to the well-defined hierarchical structure and subsequent production of densely stacked nanopetals, the ternary Mo_{0.85}W_{0.15}S₂ composition possesses an abundant number of active sites for the HER activity with the Tafel slope of 89 mV/dec. The theoretical (DFT) calculations used to simulate the band gap of MoWS₂ (0.88 eV), which is found to be less than that of MoS₂ (1.14 eV), and the directional transfer of W atoms result in an “electron-rich” configuration. The electronic-rich configuration is asserted to lower the charge transfer resistance, thereby increasing its conductivity towards the H₂ production [134,135]. Similarly, sulfur-deficient composition-graded MoWS_x is fabricated using electrodeposition, as shown in Figure 11. Two distinct compositions of the ternary Mo_xW_(1-x)S_x has been achieved depending on whether the deposition takes place either in the cathode or anode in the electrochemical deposition. Among the two distinct compositions, the ternary TMCs (Mo_xW_(1-x)S_x) fabricated via anodic electrodeposition yields higher electrocatalytic performance with an overpotential of 278 mV at 10 mA/cm² and a Tafel slope of 50.5 mV/dec. The higher electrocatalytic

performance of the ternary TMCs was attributed mostly to the even Mo/W ratio and high exposed surface area of the tiny particles [136].

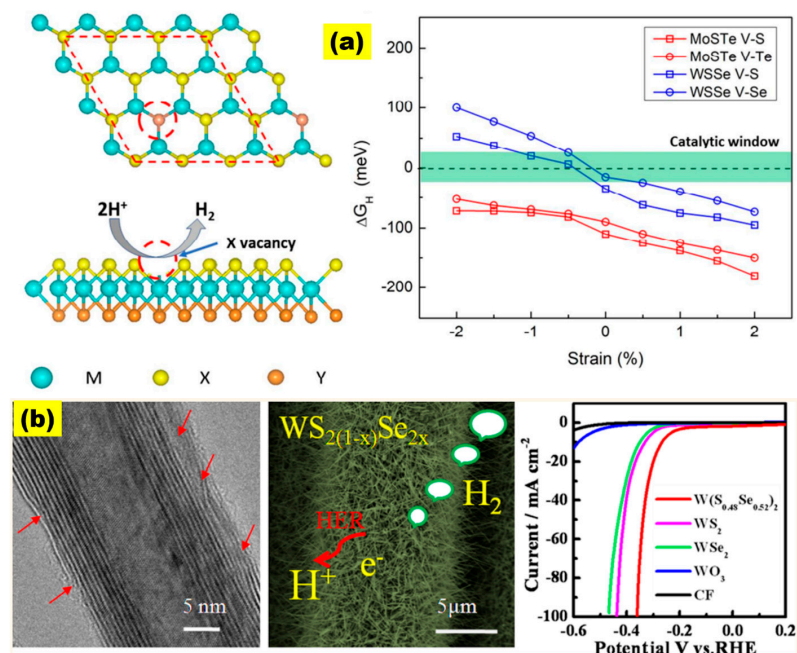


Figure 10. (a) HER reaction on Janus TMCs, and (b) ternary $WS_{2(1-x)}Se_{2x}$ nanotubes HERTEM and corresponding polarization curves [132,133]. Reproduced with permissions from Er et al., Nano Lett., American Chemical Society (ACS), 2018 and Xu et al., Nano, American Chemical Society (ACS), 2014.

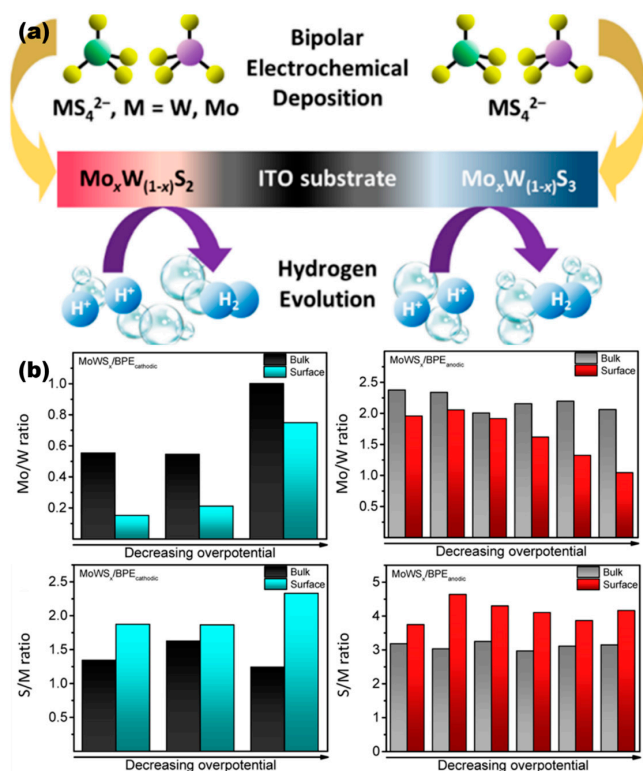


Figure 11. (a) Schematic illustration of $Mo_{1-x}W_xS_2$ and $Mo_{1-x}W_xS_3$ formation, and Mo/W and S/M ratios of (b) $MoWS_x/BPE_{cathodic}$ and $MoWS_x/BPE_{anodic}$ [136]. Reproduced with permission from Tan et al., Appl Mater Interfaces, American Chemical Society (ACS), 2017.

Meanwhile, this is not a real case applicable to all the metal cations to demonstrate enhanced catalytic efficacy. For instance, niobium (Nb) and tantalum (Ta) doping in MoS₂ and WS₂ do not show any increase in the HER activity as compared with the undoped MoS₂. However, the result points out a noteworthy discovery validating the 1T metallic phase (after cation doping) benefits in enhancing the HER activity of the electrocatalysts [137–139]. Furthermore, several computational reports on the cation dopants, including Nb and Ta with TMCs, predicted the value of ΔG_H to be nearly thermoneutral, causing benefits in H₂ production in water splitting [140]. Askari et al. produced two mixed cation systems: (i) MoWCoS and (ii) MoWCuS by a hydrothermal approach, even though they were not technically double-cation catalysts. The MoWCoS demonstrated extremely robust HER characteristics when hybridized with reduced graphene oxide (rGO), with a Tafel slope of 38 mV/dec [141]. It was asserted that the presence of CoS phases within the ternary TMCs induces additional defects and new interfaces between the phases contributing towards the enrichment of electrocatalytic activity. With numerous proposed processes (electron density modulation, 2H/1T phase transformation, morphological effects, etc.) that are accountable for performance gains, the precise role of the mixed (double) cation appears to be less evident than that of mixed (double) anion systems [141]. Thus, like mixed anion TMC-based catalysts, it is expected that a research direction will continue to be the focus on the in-depth analysis and fundamental studies on the cation dopants which will undoubtedly be helpful for the future HER research. The governance factors of the water-splitting activity of the various ternary TMC-based electrocatalysts are comparatively provided in Table 2.

Table 2. Comparison of various nanoarchitected ternary TMC-based electrocatalysts.

TMCs	Morphology	Electrolytes	Overpotential (mV)	Tafel (mV/dec)	Current Density (mA/cm ²)	TOF(s ^{−1})	C _{dl} (mF/cm ²)	Ref
Cu ₂ MoS ₄	Single-layered nanosheets	H ₂ SO ₄	96	54	10	–	–	[50]
MoSe ₂ /Cu ₂ MoS ₄	Nanodots	H ₂ SO ₄	166	74.7	10	–	–	[52]
MoS _{2-x} Se _{2(1-x)}	Nanotubes	H ₂ SO ₄	219	55	10	–	–	[61]
NiCo ₂ Se ₄	Nanowires	H ₂ SO ₄	168	49.8	10	0.453	14.9	[71]
Ni(S _{0.5} Se _{0.5}) ₂	Hollow nanospheres	Phosphate-buffered saline (PBS) solution	124	81	10	–	12.9	[73]
Mo _{37.3} S _{46.9} Se _{15.8}	Nanospheroids	N ₂ -saturated H ₂ SO ₄	93	50.1	10	0.40	9	[74]
Co-BDC/MoS ₂	2D Nanosheets	KOH	248	86	10	–	7.35	[78]
Ni-Co-MoS ₂	Nanoclusters	KOH and H ₂ SO ₄	84	96	10	–	14.6	[79]
NiCo ₂ Te ₄	Nanoclusters	PBS	80	38	10	0.65	–	[92]
Co-MoS ₂	Nanosheets	KOH	190	50.28	10	–	–	[94]
Cu@CoS _x	Hollow nanoclusters	KOH	270	61	10	–	26.9	[116]
Co ₉ S ₈ /MoS ₂	Core/shell nanocrystals	H ₂ SO ₄	97	71	10	–	23.4	[117]
NiCo ₂ S ₄	Holey nanosheets	KOH	58	122	10	0.0034	1.53	[142]
MoSe _{0.12} Te _{1.79}	Nanofilms	Ar-saturated H ₂ SO ₄	410	62	10	–	–	[129]
WS _{2(1-x)} Se _{2x}	Nanotubes	H ₂ SO ₄	298	105	10	–	1.186	[133]
ZnSe/MoSe ₂	Nanotubes	N ₂ -saturated H ₂ SO ₄	68	73	10	–	0.34	[134]
Mo _{0.85} W _{0.15} S ₂	Nanopetals	H ₂ SO ₄	250	139	10	0.168	0.70	[135]
Mo _x W _(1-x) S _x	Nanoparticles	Sulfuric acid	278	50.5	10	–	–	[136]
Mn _{0.05} Co _{0.95} Se ₂	Ultrathin nanosheets	H ₂ SO ₄	174	36	10	–	16.25	[143]
NiSe-Ni _{0.85} Se	Nanoflakes arrays	O ₂ -saturated KOH	131	98	10	–	35.9	[144]

7. Challenges and Perspective

Despite the significant and heartening improvement in the electrocatalytic (OER and HER) performance, the current development of transition metal chalcogenides (TMCs) is still in its infancy and presents numerous obstacles that restrict their practical applications. These obstacles include the need for noble metal co-catalysts to lower the HER kinetics barrier, the reliance on sacrificial reagents as hole scavengers for long-term stability, and the hitches with large-scale production. Furthermore, thorough research and in-depth comprehension of the fundamental causes and mechanisms underlying the synergistic effects of the electrocatalysts remain lacking. To achieve the pilot-scale production of H₂ fuel in the near future, the present step of TMCs in driving efficient and steady overall water splitting still has to be advanced significantly. As per the research directions, the following are offered as recommendations:

- i. In-depth examination of TMCs' intrinsic structural modifications, which includes controlled morphology to achieve the layered structures, of vacancy engineering that tends to render the electronic trapping effects, and of doping to modify the HER kinetics and the optoelectronic properties, are needed. For instance, the selective doping of p-type with n-type TMCs might result in the internal p-n homojunction formation that grants the "back-to-back" potentials between the boundaries for the improved interfacial contact;
- ii. To obtain insight into creating the highly stable TMC electrocatalysts, in-depth investigations on the OER mechanism of metal sulfides/metal selenides are necessary to comprehend the changes that occurred in the photo-corrosion kinetics and surface properties. The methods to examine the prevention of TMCs photo corrosion, such as shielding the S and/or Se atom from unnecessary exposure to the oxidizing reactant or eliminating the photogenerated holes from TMCs' valence bands (VBs) to prevent the S²⁻/Se²⁻ from self-oxidizing during the OER reactions;
- iii. To gain a thorough understanding of the principles behind the formation of ternary electrocatalysts and to reveal the underlying molecular process for water splitting, it is better to carry out the theoretical simulations and the first principle calculations on ternary electrocatalyst-based TMCs;
- iv. Diversify the research theme by increasing the variety of TMCs from the various combinations of metals to create advanced structures. Exploiting such various TMC types would create new opportunities for developing a system with the effective performance of water splitting;
- v. To solve the drawbacks of binary-layered structures, consider the possibility of creating ternary or quaternary layered systems;
- vi. Finally, a shift in the research focus needs to be realized in the developing area of pilot scaling of HER applications. To realize the expansion of HER applications, it is crucial to develop a commercially feasible water-splitting reactor with favorable macroscale configurations, and other research factors such as the impact of water pressure and process studies. Additionally, to maintain a sustainable high-yield H₂ fuel production, the TMC-based electrocatalysts' efficacy and stability must be maintained.

8. Conclusions

Electrochemical water splitting has attracted a lot of interest as a potential energy vector in future technology. Thus, effective and inexpensive electrocatalysts for overall water splitting are eagerly desired to overcome their slow reaction rate. In this review, an overview of the nanoarchitectonics of the various layered ternary transition metal chalcogenides is provided, with explanations of the electrochemistry related to the water-splitting mechanisms. To date, varieties of binary, ternary, and quaternary-based TMCs have been developed and used as electrocatalysts in water-splitting activities. Among them, the ternary TMC electrocatalysts with different chemical compositions and structures are addressed in the review. The shape, structure, and density of active sites influence the electrocatalytic activities; thus, particular attention should be paid to the precise chemical composition and morphology of the developed ternary TMC electrocatalysts. In this

regard, the different nanoarchitectonics, including single-layered, nanofibers, nanotubes, nanowires, nanospheres, and nanospheroids are provided in detail with their synthesis approach. The nanoarchitectonics ternary TMCs offer numerous active catalytic sites and high conductivity, TMCs made of tiny nanoparticles or heterostructures with conductive materials have demonstrated considerable benefits, and the use of electrodes may be a practical solution to the stability problem. It may show tremendous promise for the scaled application in the case of ternary TMCs with abundant active sites; however, greater usage of inactive basal planes needs to occur. The two main strategies being pursued to increase the TMCs catalytic activities are as follows: (i) edge engineering to expose more active sites or full utilization of catalytic potential by providing the conductive pathways (extrinsic), and (ii) chemical modification to enhance the H₂ adsorption by lowering the GH values (intrinsic) through substitution or vacancies. For further tuning the active sites for effective electrocatalytic activity, the hierarchical constructions of TMCs on self-organized nanostructures or conductive templates may be a viable method. The ease of preparation, affordability, repeatability, and stability are the major crucial aspects that need to be considered in this approach, which has a huge impact on the real-time usage of the developed catalysts. Additionally, the TMCs' intrinsic activities must be improved, and the potential strategies include the substitution of elements in the host materials. The chalcogen-atom substitution to produce chemical strain for the activation of basal planes, even if this heteroatom substitution approach has not been implemented for active edge locations of TMCs, is an excellent example of how such an effect could be achieved. To have a thorough understanding of the effective electrocatalytic activity, further research into substitution close to the active edge locations of TMCs is still required. The area of electrochemical water-splitting employing ternary TMCs as electrocatalysts has recently seen a renaissance due to the desire for renewable energy. As a result, much work still needs to be done to widen the search for high-performance electrocatalysts and to investigate the actual applications of effective advanced electrocatalysts.

Author Contributions: Conceptualization: A.A. and R.V.M.; Methodology: A.A., P.K.M., R.C. and R.V.M.; Formal Analysis: A.A., R.V.M. and A.T.Z.; Investigation: A.A., R.C. and R.V.M.; Writing-original draft preparation: A.A., R.C. and R.V.M.; Writing-review and editing: A.A., P.K.M., R.C., A.T.Z. and R.V.M.; Supervision: A.A. and R.V.M.; Funding Acquisition: A.A. and R.V.M. All authors have read and agreed to the published version of the manuscript.

Funding: The authors A.A. and R.V.M. acknowledge the ANID-FONDECYT Project No. 3200076, Universidad Adolfo Ibáñez, Santiago, Chile, for its financial support.

Acknowledgments: The author A.A. thanks the Universidad de Atacama, Copiapó, Chile for its support.

Conflicts of Interest: The authors declare no conflict of interests in this work.

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