This article emphasizes on structure-property engineering of phase-based materials for redox reactive energy conversion and environment decontamination nanosystems which are crucial in achieving a feasible and sustainable energy and environment treatment technology. An exhaustive overview for redox reaction processes, including electrocatalysis, photocatalysis and photoelectrocatalysis have been addressed. With applied in those redox reactions, we have constructively reviewed and discussed how structural-phase engineering (SPE) strategies can influence the catalytic activity, selectivity and stability. As observed, much progress has been received up to date in SPE for catalytic redox reaction improvement. However, numbers of unresolved issues to be discussed, including solar photons to excitons conversion efficiency, excitons dissociation to active reductive/oxidative electrons/holes, dual-to-multi phase-junctions, selective adsorption/desorption, performance stability and sustainability, etc., are still remained to be most intriguing as yet. We conclude by highlighting key challenges and prospects with SPE assisted redox reactions system, where the further development into the advanced engineering of phase-based materials will accelerate the sustainable (active, reliable and scalable) production of valuable chemicals and energy as well as environment treatment.

Materials’ properties are dependent on chemical stoichiometry. However, the performance of materials is significantly related to crystalline structure. Nano-to-atomic structural-phase engineering (SPE) is emerging as a new research interest in development of functions-orientated new phase materials for energy and environmental applications. Concurrently, the pressing global energy and environmental issues have driven the scientific community to identify active, reliable and scalable energy technologies with minimal environmental contamination. Far from fossil fuel-based energy technology with environmental issues, redox-reactions based energy conversion from water splitting and carbon dioxide reductions will play a significant role in sustainable energy and clean environment. With both academic and industrial interests in redox reactions for energy and environmental technologies, ideal catalysts for target redox reactions with superior sustainability, selectivity, reactivity and endurability are the keys.

SPE is becoming the well-known approach in tuning and architect the physical and chemical properties of materials of interests at atomic level [1, 2]. As the efforts continued in materials science fields, the studies of SPE grew brighter in the hope catching the innate catalytic activities of the materials due to the electronic configuration change. While we have known for a long time that there are so many compounds which show various phase(s) by differing in structures and are significantly promising in increasing the materials activity and efficiency for particular system of interest [1, 3]. The variation in crystal structure is known as polymorphism/phases. The different phases give them extra rhythm in tuning their functional properties from their size, shape and composition perspective [4]. By doing so, one can design a material with heightened electronic, optoelectronic and catalytic properties [5]. Much of that role is likely to be given over to the SPE techniques which could be potential enough to realize the improved electrocatalytic [6], photoelectrocatalytic [7, 8], photocatalytic [8, 9] and environmental degradation [10] performance in the context of desired end yields. And that SPE techniques appear to have hooked up a lot more fundamental understandings, especially in energy conversion, from water splitting to carbon dioxide reduction to environmental pollutants treatments. During these energy conversion processes, there are numbers of redox reactions such as EC-HER, EC-ORR, EC-OER and EC-OWS, PC-HER and PC-OWS, PEC-OWS, EC-CRR, and PC-CRR have been observed for many years [11, 12].

Apart from energy conversion and storage, SPE holds important applications in environmental remediation to realize a sustainable future [13]. Removing persistent organic pollutants in wastewater which has posed a serious threat to the well-being of mankind and wildlife, serves as a primary branch of environmental science [14]. Considering the diverse features of the contaminant, various treatments technologies have been explored, such as incineration, chemical oxidation, adsorption, and bioenvironmental processes [15]. There are limited reports about optimizing the efficiency of these kinds of treatments methods through phase engineering. Alternatively, most of the organic pollutant can be removed via a unique class of oxygenolysis technique known as advanced oxidation processes (AOPs) [16]. Based on the driving force for the production of ROS during the above processes, AOPs can fall into the following categories: photochemical, electrochemical, photoelectrochemical and Fenton-like advanced oxidation process, which can be commonly named as PC-AOPs, EC-AOPs, PEC-AOPs and FAOPs respectively. All of these AOPs techniques constitutes encouraging, practical and environmental-friendly means to remove persistent organic pollutants from water.

We, herein, aim at the review of SPE of materials which is likely to be involved in redox reactions like EC-HER, EC-ORR, EC-OER, EC-OWS, PC-HER, PC-OWS, PEC-OWS, PC-CRR, EC-AOPs, PC-AOPs, PEC-AOPs and FAOPs etc., and how these materials perform in terms of redox reactivity, selectivity and stability under the effects from single or multiple factors, including crystallination, defects, bandgaps, excitation photons, neutral excitons, charged carriers (e-/h+), carrier mobility, interfacial band alignment, redox species, and redox potential, etc. To improve the redox reaction dynamics, phase-based materials have been employed, however, their synergistic relationship between SPE materials and redox reactivity remain elusive yet. A systematic and in-depth understanding is needed to fully exploit the SPE advantages on the redox reactions in order to influence the overall efficiency of the energy processes. Additionally, such understandings would also be beneficiary in the development of highly active catalytic nanomaterials for redox reactions like NRR (nitrogen reduction reaction) because they have potential in producing value-added chemicals and fuels in a sustainable manner. The SPE offers a versatile and efficient way to improving the catalytic materials with facile characteristics which are the linchpin for modern energy technologies.

The occurrence of redox reactions during electrocatalytic, photocatalytic, photoelectrocatalytic, and environmental treatment processes is obvious, and these processes are of great importance. Depending on the choice of processes and experimental conditions, number of redox reactions such as EC-HER, EC-ORR, EC-OER, EC-OWS, PC-HER, PC-OWS, PEC-OWS, PC-CRR, EC-AOPs, PC-AOPs, PEC-AOPs and FAOPs are evolved, those become the central subjects of interest, particularly when evaluating the effectiveness of that processes. Of these reactions, EC-HER and EC-OER have been received much attention in recent years when one has interest in energy processes. Limitations associated with that EC-HER and EC-OER are the sluggish kinetics and overall energy lose phenomena and thereby, influencing the overall efficiency of these processes [17, 18]. The combination of these two half reactions introduce the EC-OWS reaction, another highly energy –intensive process is also on the front line of energy conversion related discussions now-a-days [19]. In back ward, these two half reactions are often known as EC-HOR and EC-ORR since the whole reactions package happens in close proximity on catalytic surfaces and/or interfaces, however, consideration should be given on the nature and selectivity of the reaction [20]. Other than these two half reactions, PC-CRR is realized to be more promising and fascinating pathways in producing value-added chemical compounds because the process mimicking the natural photosynthesis process. Undoubtedly, energy conversion from environmental pollutants like CO2 in presence of light is not only giving an extra benefit to that photocatalytic process but reducing the dependency on fossil fuels is also a major hike in achieving effective energy producing processes. Indeed, PC-CRR for manufacturing fuels like methane, methanol, ethanol, and so on, has been studied for many years and remarkable advancements have revealed such that one may able to investigate them further, even the process itself chose multi-electrons complex reduction pathways. Unlike energy processes, the environmental treatment has been employed the AOPs as water treatment processes conducted under mild conditions (room temperature and standard pressure) and based on the in situ formation of a series of highly reactive oxygen species (ROS) at an adequate concentration to efficiently remove the contaminants [21]. AOPs processes over phase materials is gaining interest very recently, while the significant advancement in this field yet to be searchable.

From surface reactivity perspective, all of these redox reactions suffer from low efficiency because the dynamics of the reactions, and the synergistic interplay on catalysts surface. In electrocatalytic process, for example, the EC-HER is highly sensitive to the catalytic surface in basic environments while it is not easily understandable on its insensitivity towards the catalytic surface in acidic medium [17]. Additionally, the EC-OER is equipped with over-potential issues and insufficient in lessening the energy loss for that process. In parallel with this unsatisfied catalytic surface activities, the PC-CRR on catalyst surface or interfaces dictates much complexity since such process involves more reductive/oxidative electrons/holes, more intermediate redox species and hence more hydrogenation/oxygenation steps, besides the common generation-recombination issues from photoinduced electron-hole pairs for other redox processes. Although previous studies have indicated that the process performances can be improved by means of tuning the structure of the catalysts, which inherently works as catalytic active sites for the reactant molecules [22]. Degradation of major pollutants from the water is a key research over the phase materials while how phase engineering affects the activity of the catalysts for pollutants degradation is still complicated. Specifically, the dynamics towards the ROS activation occurring at the solid/liquid interface of various phases is unclear. In order to achieve highly active and long-lived catalysts, one can pick up the idea that structural engineering at atomic scale could open new vistas in attaining high performance as well efficiency because such phase engineering approaches not only change its electronic structure but disclose improved physical, optoelectronic and hence catalytic properties.

Motivated by the above phase-based materials capability for redox reactive energy conversion and environmental treatments, we would envision to speculate an overview of structural phase engineering at nano-to-atomic scale regimes and how such SPE could influence the respective energy conversion processes. Readers need to be cautious that we do not summarize here many other excellent published articles simply because of the scope and purpose of this manuscript [23, 24]. In line with this, we divide our articles in number of sections where a comprehensive phase materials and its activity cover in section 2, the electrochemical redox reactions on SPE cover in section 3.1, while 3.2 sections highlight the photocatalytic and photoelectrocatalysis of water, and section 3.3 covers the photocatalysis of CO2 and section 4 emphasizes on environmental treatment. And the end, we speculate some key gaps that need to be investigate further in improving the catalytic efficiency for energy conversion and environmental treatment processes.

There are numbers of materials in nature those have more than one crystalline structure which are known as polymorphism/phases. Phase transition can be experienced from different synthetic methods: ion intercalation [25] doping/alloying [26], thermal activation [27],  strain engineering [28], defect engineering [29], electrostatic gating [30], charging [31] and pressure induced treatment [32]. Each of these techniques has its own merits and potential to change the phase from one to other. Nevertheless, as yet the transition metal dichalcogenides (TMDs), noble metals (e.g., Pt, Rh, Ag, Au, Ir and Ru), SnS2, SnS, GaAs and InAs, are reported to be shown the phases [33, 34]. Generally, most of the pure metals in periodic table may adopt one of the three possible structures: fcc, hcp or bcc structures. With increasing the atomic number in the transition metal series, the elements show the structural sequence of hcp ~bcc~hcp~fcc [35]. This conclusion is supported by the relative stability of these phases in metals what fundamentally determined by the total energy of these phases. When the structure of the metals is changed, the degree of orbital overlap between d orbitals is also changed that actually controls the electronic band structure, DOS shape, and total energy of the metals and such properties also be different for different phases [35]. It is important to keep in mind that the phase transition from stable bulk phase to another is highly dependent on the temperature-pressure relationship for the corresponding reactions. It is reported that several metals such as Fe, Au, Ag, and Ru shows different phases than their stable bulk phase. For example, Fe has ferromagnetic bcc structures while its transformative phase is non-magnetic fcc structure. Bulk Ru has hcp structure while both bulk Au and Ag have fcc structure [35]. Noble metals show hexagonal, tetragonal and cubic phases; of these phases, the thermodynamically less stable phases exhibit unusual physical features and excellent catalytic properties [36, 37].

Other than above categories, the phases of NbSe2, TaSe2, TaS2, and TiS2 are also highlighted, those prone to show either 2H or 1T phase [33] while ReS2 shows distorted 1T phase [38]. TMDs is a paradigm of 2H (hexagonal), 1H (trigonal prismatic), 1T (octahedral), 1Tʹ (monoclinic), Td (orthorhombic) and 3R (rhombohedral) phases [3] while SnS2 and SnS reveals cubic, trigonal, hexagonal and orthorhombic structure along with phase-dependent electronic band structure and dopant type [33]. TiO2 is one of the most frequently studied photoactive materials which possess three polymorphs such as anatase, rutile and brookite with different electronic band structures [39]. Another oxide material, BiVO4 shows monoclinic and tetragonal phases with differences in lattice structures [40], while CdS appears with cubic, and hexagonal phases [41]. TMDs materials are well-studied materials for its ability to display different phases; MoS2 and WS2 are the most two known materials among them while consideration is equally given to other TMDs materials such as MoSe2, MoTe2, WTe2, WSe2, ReS2, Pd2Se3, NbS2, etc. what have been emerged as new class of layered materials for photocatalytic and electrochemical reactions [42-44]. Since there are numbers of phase materials, and each phase have different ability to play role for respective reactions. Therefore, we do not cover possible all phases for all elements here inclusively rather we prepare a library for phase materials where at least one phase examined in any of the above redox reactions. In order to present an overview to the reader, we have been trying to tabulate the different crystal phase materials in Figure 1, which we do believe are the up to date and no report alike this has been published yet.

Many materials have different polymorphs or phases in nature. Variation of the phases for the same materials arise from the change of electronic structure, which is also the primary reasons for different performances for phase to phase. Taking MoS2 as an example that shows three different phases where 1T phase is believed to be more conductive than its 2H phase as do their performances in forming hydrogen [50]. Chou and colleagues [51] have demonstrated that for HER system, the 1Tʹ-MoS2 phase is more active than that of 2H phase because the active sites are spread over both edges and basal planes while the distribution of active sites is only on the edges of 2H-MoS2 phase. Another example in this regard is the TiO2, which have anatase, rutile and brookite phases. Among these phases, the brookite phase is reported to be provide the highest efficiency in terms of product formations during PC-CRR [52]. This verifies the importance of different phases on the reactions like above and on the process efficiency as well. To gain increased activity over the catalytic materials, it is therefore crucial to design and architect such phases structurally towards the atomic scale regime.

Working with phase engineering brings up innate properties for the desired processes. Du and co-worker [53] have pointed out that the photocatalytic hydrogen evolution under visible light irradiation could increase by a factor of 35 over the optimized 1T-MoS2/CdS NRs hybrid system as compared with the pure CdS NRs system. Such improvement subjected to the variation of the phase 1T- MoS2 nanosheets. In parallel, Enyashin and colleagues have [54] fabricated the 1T-MoS2 phase within WS2 nanotubes along with rhenium (Re) doping which led to stabilize the 1T-phase more profoundly as compared with the lattice of the alkali intercalated compound. Indeed, the alkali intercalation have erroneous effects on phase transition since the transferred electrons from alkali metals would possibly enhance the electron density of the d-orbital of transition metal, leading in destabilization of 2H phase and its conversion either in metallic 1T or distorted 1Tʹ phase [55].

The metallic 1T/1Tʹ phase display superior HER activity than the 2H phase while the thermodynamically driven reverse phase transition into 2H phase causes nondurable HER performance. To further understand how durability can increase the HER performance, Liu and co-workers [56] have synthesized 1Tʹ phase mixed with 2H- WS2 phase (1Tʹ-D WS2) and pure 2H- WS2 phase via a facile and effective one-pot colloidal method. The HER activity is far superior on 1Tʹ-D WS2 samples over 2H- WS2 phase, showing an overpotential of 200 mV at 10 mA/cm2 along with 50.4 mV/dec of Tafel slope. In acidic medium, the stability test discloses the endurance half-life is about 46 days under constant overpotential of 0.3 V and at 41 mA/cm2, even vigorous erosion arises from continuous hydrogen bubbling, which put excess capillary stresses on the atomic sheets.

Of the few reports that established that the functional characteristics of noble metal nanostructures can also be tuned because of their varying crystal phase, shape, composition and size, the Ag elements with 4H phase show 100 times higher in-plane resistivity and improved visible-light absorption capacity than those fcc (face-centered cubic) phase Ag films [57]. Through phase conversion from fcc to fct (face-centered tetragonal), the FePt nanoparticles display a transitional phenomenon from superparamagnetic to strongly ferromagnetic [58]. In a similar approach, using solution-phase epitaxial growth under ambient conditions, the unusual 4H hexagonal Ir, Rh, Os, Ru and Cu nanostructures coupled with 4H Au nanoribbons (NRBs) while 4H Au NRBs transform phase from 4H to fcc [59, 60].

Gao and colleagues [61] have studied the phase transition of single layer MoS2 from bulk 2H to metallic 1T and then to 1Tʹ phases and show how this transition impact on the HER activity from the density functional theory viewpoint. The phase transition starts by transferring S atoms from one pyramidal position to the other pyramidal position of the unit cell. Figure 2 exhibits the phase transition of 2H to 1T under charge states from 0 e- - to- 4e- in each MoS2. The relative energy of neutral state (0.8 eV) and 1e- charge state (0.31 eV) reduces from positive to negative for -0.05 eV of 2e−, -0.10 eV of 3e−, and -0.3 eV of 4e− charge states. This implies that the charge injection could stabilize the 1T-MoS2, especially for the case where more than 1e- is involved, then 1T-MoS2 is more stable than its bulk counterparts. The phase transformation energy barrier also reduces to 1.11, 0.71, 0.54, and 0.27 eV in charge states of 1e−, 2e−, 3e−, and 4e−, respectively, from 1.59 eV in neutral state. Too precisely, the negative charge inducing 2H-MoS2 convert into 1T-MoS2 easily. The HER follows two major reactions step namely Volmer and Heyrovsky reactions (we will discuss them in next section). Based on the Gibbs free energy calculations as shown in Figure 2, it is emphasized that 1Tʹ-MoS2 shows superior catalytic activity.

It is suggested that SPE influences the reaction activity, performances and efficiency for organic pollutant degradation. The metal oxides with inactive OER property, such as tin dioxide (SnO2), lead dioxide (PbO2), are generally suited to act as the effective catalysts or substrates for electrochemical pollution oxidation, where the OER side reaction is suppressed. Many techniques such as anodic or cathodic deposition, have been directed to obtain different phases of metal oxides [62]. Abaci and colleagues have investigated the performance on different phases of PbO2 towards electrochemical phenol degradation [63]. By changing the precursor concentration and deposition current density, films of pure α-PbO2 and β-PbO2 were obtained, respectively. Consequently, the higher conductivity, superior stability and unique porous structure endowed β-PbO2 with higher HO• flux and faster oxygen atom transfer, resulting in the better performance than α-PbO2 in phenol degradation. The feasibility of different phases in nontoxic metal oxides (e.g. MnO2, WO3) are also explored for environmental electrocatalysis. With its abundant sources, MnO2 has been broadly used as electrode matirial for electrochemical application. Devaraj and Munichandraiah [64] investigated the specific electrochemical capacitance of three MnO2 phases, which followed the order as: α- MnO2 > γ-MnO2 > β-MnO2, suggesting that they possess different electrocatalytic activities.

Energy conversion processes such as electrocatalysis, photocatalysis and photoelectrocatalysis has been studied for many years to identify reliable and scalable energy carriers like hydrogen or other valuable chemicals. Neither a single process nor their combination can produce industrial grade energy fuels yet, even though much remarkable advancement and progress over these processes has been reported [23]. These energy processes need to be translated into productive means by utilizing cheaper and environmentally benign resources. One of the characteristics of these energy processes is the involvement of either oxidation or reduction reaction, or combination of multi-electron process. We recall them as redox reactions that apparently kinetically slow reactions and require much energy input to drive them in forward [28]. Historically in such a case, we have seen that materials from noble metals group is likely potential to reduce energy barrier and hence, accelerate the redox reaction into the direction of targeted products [23]. Owing to their high cost and scarcity, it is not viable to use them in large scale applications. Therefore, a new window is opened for the other materials but to be competitive for those redox reactions, they should come with extended electronic structure and optoelectronic properties. As we have observed from our previous section that there are numbers of such materials those possess alternating lattice structure and thus, able to form various atomic arrangement at nano regime known as phases or polymorphs.

Very recently, many research groups have examined different phase-based materials in energy production using redox reaction such as EC-HER, EC-OER, EC-OWS, and PC-CRR. Taking orthorhombic and cubic phases of CoSe2 electrocatalysts as an example, it was shown that the cubic phase was outperformed the orthorhombic phase because the increased electron mobility which facilitates the intrinsic catalytic activity of that phase for HER processes [65]. Another example is the 1T-MoS2 phase materials which are believed to be possess reactive sites at both basal plane and edges that makes them excellent candidate over other phase (2H-MoS2) in HER system. Presence of large number of active sites, it can extend its electron mobility in order to reduce the energy barrier for redox HER system. While the examination of the single phase for electrocatalytic HER system is continuously surge, the construction of the multiple phases such as 1T/2H-MoS2 could be more effective in achieving higher electrocatalytic performance. Among many reasons for such improvement in electrocatalysis, the interfacial charge transfer is one which can increase the electron mobility faster because of the intimate contact between them.

Application of phase materials in both photocatalysis and photoelectrocatalysis processes have been reported over the decades since both of them provide great advantages in the context of using abundant, cheaper and environmentally friendly resources like solar energy while producing substantial volume of the end products. However, both processes mingled with complication arising from reaction kinetics and dynamics [66, 67]. The overall water splitting with the aid of light illumination is considered one of the potential approaches in evaluating both HER and OER processes simultaneously. To be specific in such a case, many research groups employed phase junction of α-Ga2O3 and β-Ga2O3 and found that the photocatalytic performance was higher than other phase junction like γ-Ga2O3 to β-Ga2O3. Another classic photocatalytic process is the reduction of CO2 into valuable chemical fuels, which has been scrutinized over different crystal phases materials-TiO2 is one of them. TiO2 has three distinguish phases such as anatase, rutile and brookite which are believed to be effective for different redox reactions [68]. Nevertheless, we can say that in the search of scalable and reproduceable energy processes, it would be very fascinating to use different phase materials since they have alternating electronic band structures.

There are limited reports about optimizing the efficiency of the pollutants treatments processes through phase engineering. For example, Cao et al. introduced a concept of structural design for the synthesis of hierarchical core/shell MnO2 ellipsoids comprising of multi-phase [69]. The porous γ-MnO2 core coupled with the active edges exposed on the irregular-shaped, upright-standing nanoflakes of α-MnO2 shell resulted in high adsorption capacity on methylene blue. Karunakaran et al [10] quantified and compared the antibacterial activity of functionalized 2H- and 1T-MoS2. The 2H-MoS2 demonstrated better antibacterial activity than that of the 1T-MoS2. On the one hand, the semiconducting 2H-MoS2 possessed improved oxidative stress. Besides, the unique synergistic effect of 2H phase and the functionalized ligands, was responsible for the membrane damage and hence resulting in enhanced activity. Although these traditional methods show robust efficiency, they cannot degrade the pollutant selectively or cause secondary pollution if the processing conditions are not well controlled [70].

Electrocatalytic water splitting has been thought to be a viable pathway in producing hydrogen as well as oxygen. There is a growing interest in developing promising phase-based electrocatalytic materials toward cost-effective water splitting process and the research in this field has been intensified over the last decades. One of the benefits in using the SPE in water splitting is to regulate the adsorption energies of atomic hydrogen or OER intermediates like OH\*, O\*, and OOH\* onto the surface of the phase materials so does the improvement in HER or OER activity [23]. Possible reason is the alteration in electronic structure in the phases which play key role in providing the reactive sites for the reactant molecules. In the following section, we will cover various phase materials in water splitting system those are believed to be effective and applicable for the respective redox reactions. In addition, we will speculate more about structural phase based engineered materials for electrocatalytic driven HER in below while at the end of this section, we summarize (Table 1) some recent literature outcomes in that research arena.

Hydrogen production from electrochemical water splitting consider an ideal eco-friendly approach [17]. HER occurs at one side electrode while OER experiences on the other side. These distinctively different reactions have thermodynamic importance in optimizing the desired outcomes. Yet the key contributions for HER come from an effective electrode that works as an electrocatalyst, which has ability to convert the pair of protons and electrons into H2. The classic HER involves multi-step reactions including adsorption, reduction, and desorption processes. In acidic environment, the elementary steps and overall reaction pathways would be as follows [71]:

In acidic environment, the adsorption of hydrogen comes from hydronium ion while in alkaline environment, it relates with water molecule dissociation. Regardless of experimental conditions, the step is referred to as Volmer step. The conjugation of the adsorbed hydrogen (Had) to form molecular hydrogen is realized through either a Heyrovsky or Tafel step. Performance of HER electrocatalysts is largely dependent on the inherent chemical and electronic properties of the electrode surface where performance evaluation of HER is seeking to understand the kinetics and reaction rate for that electrocatalysts. To get such information, one can use Tafel slopes which directly linked with reaction steps. Setting the rate limiting rules, one should able to identify that whether the reaction is Volmer step (in this case, the hydrogen adsorption energy is too weak) or Heyrovsky or Tafel step (the hydrogen adsorption energy is too strong) controlled. However, the performance for HER from that rate limiting concept could provide poor apparent activity, which therefore make an urgency of volcano shape plot (Figure 3) demonstrator to evaluate the true HER activities-a quantitative relationship between thermodynamic overpotential and the free energy of hydrogen adsorption energy [72, 73]. By using volcano plot, it is easy to understand that how an ideal catalyst would be look like because at Zero Gibbs free energy position it would give highest exchange current density that is to say that an ideal catalyst neither binds reaction intermediates too strongly nor too weakly. In determining HER activities, however, alkaline conditions are more complicated than that of acidic media because the evolution both of H and OH species due to water dissociation processes [74]. Therefore, the careful assessment is of significant importance for HER by considering the solution pH, solvation effects, electrode potential, and electric double layer effects [75]. These identifying parameters help to evaluate the activity and performance of the catalysts for HER where any other parametric evaluation, however, deserve to be investigated.

As a great way to improve the catalytic active sites and enhance the intrinsic activity for HER, the SPE can reveal the true activity of the either basal planes or exposed edge sites or their coupling contributions to HER under systematic experimental setup. Upon displaying their preferential active sites, the performances of the HER can be as high as possible. MoS2, a classic example of 2D materials, show phases-1T and 2H, among many others. Switching between 2H and 1T phases of MoS2 materials might be sound counter-intuitive in designing and fabricating catalytically active materials because these phase structures unlock the instinctive properties. Let us take 1T-MoS2 phase as an example, which expected to be 107 times more conductive than the 2H phase and likely to show better performance in producing hydrogen [50]. The HER activity is found to be interlinked with hydrogen adsorption free energy, which is much higher for 2H-MoS2 phase rather than 1T-MoS2 phase that also an illustration of kinetic energy barrier for HER [12]. In the case of 1T-MoS2 phase, the energy needed for H binding to the S sites is largely dependent on the quantity of H coverage [76]. The synthetic approaches, however, have a much cleaner effect in realizing SPE strategy whether it might be the combination of preferred phase(s) with preferred nanostructuring, which led to improve HER performances. Taking intercalation of lithium ions into the van der Waals gap of MoS2, a phase transformation from semiconducting 2H to metallic 1T phase was observed while a vertically aligned MoS2 electrocatalytic nanofilm was believed to be reasons for enhanced catalytic performances (Figure 4) [6]. Lithium intercalation potential play vital role in expanding the van der Waals gap until exfoliation completion where potential drives from high to low with MoS2 nanofilms.

SPE with chemical exfoliation can convert the phase from 2H to 1T phase of MoS2 because the electrons move to the MoS2 nanosheets from the alkali atoms where this electron fill up the lower-lying MoS2 orbital that stabilize the 1T phase and destabilize the 2H phase [77]. Applied characterization techniques and electrochemical studies confirmed that the 1T-MoS2 nanosheets showed facile electrode kinetics, improved electron transport, and increased density of catalytic active sites, that increase both intrinsic catalytic activity and overall catalytic performance. The estimated overpotential and Tafel slope were found to be -187 mV at 10 mA cm-2 and 43 mV dec-1, respectively, over the as-prepared 1T-MoS2 nanostructure while the un-exfoliated MoS2 corresponds to the overpotential of -320 mV at 10 mA cm-2 and Tafel slope of 110 mV dec-1. They have argued that making active basal plane of 1T -MoS2 for inherent catalytic activity is needed more than creating active edge sites for catalytic activity of 2H- MoS2 because the basal plane has more exposed surface areas. The volume of 1T-phase in MoS2 is important here because the HER activity is related with that 1T-phase quantity [78]. As compared with chemical exfoliation in solution utilizing n-butyllithium, the lithium borohydride exfoliation gives high content of 1T phase (80%) while former one corresponds to 50% content of 1T phase. A low overpotential of 100 mV at 10 mA cm-2 and small Tafel slope of 40 mV dec-1 were reported over the glassy carbon supported 1T-MoS2 phase. They also highlighted that the oxidation of edge sites of 2H- MoS2 noticeably decrease the electrochemical activity wherein the oxidation of 1T -MoS2 doesn’t reduce the HER performance. This imply that the phase transition from 2H to 1T phase could enhance the number of active sites on the basal plane along with edge site that potential to accelerate the HER activity. This study infers that the catalytic active sites of 1T-MoS2 could be found on both edges’ sites and basal plane while this could be different in case of 2H-MoS2 phase. The chemical exfoliation, however, for transforming the phase and tuning the electronic structure is not the only way today because there are more novel and facile methods continuously investigated.

Structurally, 1T phase stacked in-plane on the 2H phase that known to have outstanding HER activity while SPE of other active sites can be a prominent way to enhance the HER performance. To this end, the vertically growth of 1T phase on 2H phase was reported to be shown higher electrochemical activity of HER [79]. The calculated Tafel slope of 42 mVdec-1 along with a relatively low overpotential of 116 mV at 10 mAcm-2 was remarked. Here, the basal plane of MoS2 is presumably catalytically inactive wherein the exposed fractal-shaped single layer MoS2 can increase the electrocatalytic HER activity because the fractal-shaped single layer MoS2 have unique electronic structure and local stoichiometry which enhance the edge to substrate ratio-a desired characteristics for an improved HER performance. Additionally, the d-band theory implies that the electron supply to the catalytic active sites increases due to the tensile strain in MoS2 which thus boost the electrocatalytic HER activity [80]. Likewise, Wan and co-workers [81] have prepared fractal shaped single layer MoS2 along with large tensile strain on fused silica via chemical vapour deposition (CVD) route and reported that the as-synthesised MoS2 have a large amount of exposed edge sites which is beneficial for superior HER activity as compared with triangle-shaped MoS2 on SiO2 substrate. A low overpotential of 185 mV at a current density of 10 mAcm-2, a Tafel slope of 45 mVdec-1 and an exchange current density of 50.9 μAcm−2 was obtained with fractal-shaped single layer MoS2 electrocatalysts which correlates with an edge-to-substrate ratio of about 0.33 μm−1. It is likely that the electron supply to the catalytic active sites was rapid due to large tensile strain. One disadvantages of this approach is that the formation of catalytically active edge sites is thermodynamically unfavourable rather than its basal plane. Being identical to 1T-MoS2, the 1T-WS2 nanosheets predict to be shown an improved HER catalytic activity [12]. The 1T-WS2 nanosheets can be synthesized with the aid of CVD grown 2H-WS2 nanoflakes by means of microwave-assisted n-butyllithium intercalation method [12] or either from commercial 2H-WS2 particles. The concomitant transformation and exfoliation of 2H-WS2 phase into 1T-WS2 nanosheets show improved electrical mass transport, facile electrode dynamics and enhancement in catalytic active sites [12]. Differing in starting 2H-WS2 samples for these two studies could reasonably end up with significant differences in terms of catalytic HER performance [12]. As compared with bulk WS2, the CVD assisted WS2 nanoflakes exhibit high density of sulphur vacancy result in higher performance for HER.

Theoretical analyses presenting that the sulfur defects and more exposed edge sites on 1T- MoS2 phase could enhance the electrocatalytic performance. Based on that ideas, Yin and colleagues [82] have prepared multiphasic MoS2 that contains several sulfur defects and active sites and showing that both sulfur defects and exposed sites significantly increase the electron conductivity which hence leading to high HER activity. Since sulfur vacancies are catalytically active, the authors could effectively fine-tune the hydrogen adsorption free energy and catalytic activity of MoS2 by means of manipulating the alliance of sulfur vacancies and strain sites. Briefly, they have prepared mesoporous 1T-phase MoS2 nanosheets (P-1T-MoS2) with the aid of liquid ammonia lithiation approach to evaluate the crystal structure, edges, and S vacancies to the catalytic activity for HER. To make the concise evaluation of the calculated values, they have chosen four other samples namely mesoporous 2H phase (P-2H-MoS2), mesoporous 2H-phase MoS2 after sulfur compensation (P-2H-MoS2+S), 1T-phase MoS2 (1T-MoS2), and 2H-phase MoS2 (2H-MoS2) (Figure 5). The key findings include the superior HER catalytic activity over 1T-MoS2 and P-1T-MoS2 phase as compared with 2H phase; and (ii) the P-1T-MoS2 and P-2H-MoS2 materials show enhanced catalytic performance over that bulk materials because the abundance of the edge-terminated features in those samples which ensure an isotropic electron transport; while the P-1T-MoS2 sample have more edges than the conventional 1T-MoS2 phase which represents a better performance; and the S vacancies have significant effect on the HER catalysis as evidenced from the low overpotential of P-2H-MoS2+S than for P-2H-MoS2 samples. In addition, the characterization studies of those samples reveal that the synergistic effects of crystal phase, edges and S vacancies result in high intrinsic HER activity over porous 1T-MoS2 nanosheets with overpotential of 153 mV at 10 mAcm-2 and Tafel slope of 43 mV/decade. Similarly, the introduction of cracking on 1T- MoS2 nanostructure is an alternative pathway to obtain optimal number of internal active sites, that supposed to be need for achieving high performance in HER as well as high stability [83]. In order to answer the stability questions for 1T phase, a qualitative and quantitative insights into the nanostructure array is crucial and in this sense, Sun and workmates [22] have experimentally investigated the structural evolution for different type of 1T phase, for example, 16.4%, 69.4%, and 90.2% of 1T phase using bottom-up hydrothermal approach utilizing urea as a starting material. They pointed out that the growth of 1T-phase MoS2 depends on the ammonia-assisted assembly, recrystallization, and stabilization processes. An overpotential of 76 mV at 10 mAcm-2 was marked for hydrogen evolution in acidic media which shown durability up to 15 hours. Not uncommon, the unique array structure and high-purity 1T-phase MoS2 nanosheets had believed to be the reasons for that electrocatalytic HER activity. However, the phase engineering by means of hydrothermal methods, remains less understood because the introduction of guest molecules or ions which progressively effects on the long-term stability of 1T-MoS2. While making the stable 1T-MoS2 is the basic for improved HER activity, the inclusion of small molecules or ions to engineer 1T-phase MoS2 along with high purity and controlled electronic properties may be an alternative option in materials science [22]. Lai and colleagues [84] have synthesized a series of 1T′-phase ReS2xSe2(1-x) (x = 0–1) nanodots to produce hydrogen from electrochemical water splitting in acidic environment. Among the synthesized products, the 1T′-phase ReSSe nanodot shows the maximum hydrogen evolution performance along with a Tafel slope of 50.1 mV dec–1 and a low overpotential of 84 mV at current density of 10 mA cm–2. The asymmetric sulphur vacancy in the highly asymmetric 1T′ crystal structure promotes the optimal hydrogen absorption energy of active sites, which results in excellent hydrogen evolution activity and excellent long-term durability.

Theoretical and experimental studies infer that the natural semiconducting 2H phase could be electrocatalytically active since it has the unsaturated X-edges and have almost zero Gibbs free energy for H adsorption [85]. Soon after, such findings become the motivation for the development of many nanostructured electrocatalytic materials, which intentionally exposed the edge sites leading to improve HER electrocatalytic activity. By engineering and designing of a single and/or few layered 2D- heterostructures, Najafi and colleagues [85] synthesized single and/or few layer MoSe2 flakes over graphene or single-wall carbon nanotube via solution method that however, increase the number of electrocatalytic sites. In activating the basal plane of 2D materials, they used thermally induced texturization by annealing the MoSe2 flakes in a hydrogen environment while a chemical bathing in an organolithium compound can change the 2H phase of MoSe2 to 1T phase of MoSe2. A cathodic current density of 10 mAcm-2 at overpotential of 100 mV, an exchange current density of 0.203 µAcm-2 and a Tafel slope of 63 mVdec-1 reported over the MoSe2 flakes and their electrode assembly for a given mass loading. However, a 4.8-fold enhancement of the exchange current density and a reduction in the Tafel slope of 54 mVdec-1 observed for as-engineered electrodes. The phase conversion of MoSe2 flakes is subjected to enhance their electron conductivity and increase the surface performance of their basal plane for atomic H binding which may facilitate the Volmer reaction pathway that accelerate the subsequent Heyrovsky reaction.

Nevertheless, the chemical exfoliation by means of lithium intercalation could induces the phase transition between the bulk 2H phase to metallic 1T phase which is very important for electron transportation from electrode to the active edges. Unveiling such properties from TMDs materials for enhanced electrocatalytic HER activity, Ambrosi and associates [86] have prepared 1T phase of MoS2, MoSe2, WS2, and WSe2 nanosheets using chemical exfoliation method and compared their efficiency towards hydrogen evolution rate with the corresponding 2H phases. They showed that the HER activity and degree of exfoliation are depending on various organolithium compounds utilized for intercalation, for instance, as compared to methyllithium compounds, the ter-butyllithium and n-butyllithium have more capacity to provide better HER catalytic activity and degree of exfoliation. However, an overpotential of -0.8 V at 10 mAcm-2 reported for WSe2 while it was -0.55 V for MoS2 at 10 mAcm-2. Furthermore, the WS2 and MoSe2 shows best performance for hydrogen evolution than those MoS2 and WSe2 that linked to its largest composition of 1T phase. The kinetics for these 1T phase based four TMDs materials subject to both Volmer and Heyrovsky reactions which control the HER rate. The calculated Tafel values of WS2, MoSe2, MoS2 and WSe2 are 85, 82, 99 and 4240 mVdec-1, respectively that showing the superior performance of 1T phase of WS2 and MoSe2 for hydrogen evolution over the corresponding 2H phases. In another study, Gao and colleagues [61] have shown that the kinetic energy barrier for 2H-to-1T phase transformation could be less due to the presence of negative charges on 1T-MoS2 phase while the spontantaneous phase transformation into 1Tʹ phase (distorted monolayer structure) from 1T phase might be occurred. The rapid charge-transfer dynamics assists to achieve superior HER performance for HER over 1Tʹ-MoS2 phase while its catalytic activity is comparable with that of 2H phase.

Coupling different phases is an effective pathway in increasing electrical conductivity and improving the effective catalytic active surfaces, thereby improving the HER catalytic performance. Kwak and associates [87] have prepared 1Tʹ-phase based MoS2 nanostructures by means of ammonium (A) and methylammonium (MA) intercalation synthetic method to evaluate their catalytic efficiency for the HER. Both higher catalytic activity and excellent stability over the MA intercalated 1Tʹ-MoS2 nanostructures had noticed as compared with A-intercalated 1Tʹ-MoS2. As with concentrations either A or MA, the phase conversion from 2H to 1Tʹ does climb up, which could be further accelerated by S vacancies, according to first-principles calculations. Such calculations help to corroborate the higher durability of MA –intercalated 1Tʹ-MoS2 nanostructures, proving that the repulsion between the positively charged MA moieties reduced. Yet questions remain unanswered that the phase conversion of 1T and 1Tʹ-MoS2 nanostructures using one-step hydrothermal protocols with the aid of MA, because the underlying issue of stability as we have seen in previous section. Conversely, the stability of MA intercalated 1Tʹ-MoS2 nanostructures was reported to be about six months at ambient conditions, while that of A intercalated 1Tʹ-MoS2 nanostructures transformed to the 2H phase very fast. The overpotential, and Tafel slope of MA and A intercalated 1Tʹ-MoS2 nanostructures were 0.17 V at 10 mAcm-2 and 38 mVdec-1, and 0.2 V at 10 mAcm-2 and 45 mVdec-1, respectively. The kinetic evaluation of 1Tʹ-MoS2 nanostructures exhibits the upswing patterns towards HER activity while Tafel slope indicates the two steps mechanism for HER as Volmer reaction and Heyrovsky reaction.

In another study, Kwak and associates [46] have synthesized nitrogen (N) doped 1Tʹ- MoS2 layered nanostructures using various alkyl amines namely methylamine (MA), ethylenediamine (EDA), diethylenetriamine (DETA), and triethylenetetramine (TETA) as intercalants which corresponds to 1-4 N atoms. With intercalation of amine molecules at 10 atomic%, the lattice constant expands by up to 160%. The concentration of doped N atoms increases with increasing N number in the amine, which, thus improved the catalytic HER performance. The calculated data show that all the amine intercalated N-doped MoS2 samples display excellent HER performance in the order of TETA > DETA > EDA > MA. The intercalation with TETA displays a Tafel slope of 36 mV dec−1 and 10 mA cm−2 at −160 mV (vs. RHE). Theoretical analysis disclosing that the N doping and amine intercalation enhance the density of states near the Fermi level in a narrow range and showed up an effective overlap of the dz2 (Mo), pz (S) and pz (N) states. The combination between these factors increases the electron concentration at the surface and hence the mobility for enhanced HER. It is also noted that most of the catalytic active site is S vacancies. The authors argued that the HER performance could be increased in more by controlling the amine intercalation over the MoS2 samples. Likewise, Wang and co-workers [88] have engineered the multiphasic 1T/2H-MoS2 nanostructures by means of hydrothermal approach with the introduction of ammonium bicarbonate. A plethora of exfoliated MoS2 phase observed because the preparation process contains many ions and small molecules that origins from the decompositions of the process chemicals. The synthesis variables like temperature could influence the 1T phase content in the desired polytype. As reported, the highest amount of 1T phase content achieved at optimum temperature of 200 °C. Yet the performance of HER could reduce as with synthesis temperature. This phenomenon subjected to its thermodynamically metastable character of 1T phase. With highest content of 1T phase, the as-prepared polytype reached a Tafel slope of 46 mV dec-1, inferring that the multiphasic 1T/2H-MoS2 nanostructures pave the way for improved electrocatalytic performance. Liu and colleagues [89] have prepared 4 H/fcc-Au@ MoX2 (X= Se and S) nanocomposite for electrocatalytic HER in acidic environment and reported the excellent activities with a low overpotential of 178 mV at 10 mA/cm2, a small Tafel slope of 43.3 mV/dec. The excellent activities were subjected to the high concentrations of 1Tʹ phase in the prepared MoSe2 and MoS2 monolayers. It is suggested that different crystal phases of noble multimettalic nanomaterials could boost their catalytic properties and beneficial for HER in acidic medium. Similarly, Fan and co-workers [90] have prepared three different multimettalic nanomaterials such as 4H/fcc trimetallic Au@PdAg core−shell 4H/fcc trimetallic Au@PtAg and quatermetallic Au@ PtPdAg core−shell nanoribbons (NRBs) using the 4H/fcc Au@Ag NRBs as seeds by means of galvanic reaction method under ambient conditions. Among them, the prepared 4H/fcc Au@ PdAg NRBs shows promising performances for HER with longer durability. Reported that the overpotential of that nanocomposite was about 26.2 mV and Tafel slope was 30 mV/dec, which comparable with Pt black. The synergistic interplay between their dendritic surface morphology, effects of multiple components and unique crystal structure were the major reasons for such superior electrocatalytic performance of 4H/fcc Au@ PdAg NRBs. In similar study, Zhang and co-workers [91] have prepared the well-crystalline lotus-thalamus shaped Pt-Ni anisotropic superstructures (Pt-Ni ASs) that has spatial heterogeneity of crystal structures and compositional elements. The superstructures are composed of one Ni-rich “core” with fcc phase, several Ni-rich “arms” with hcp phase protruding from the core, and facet-selectively grown Pt-rich “lotus seeds” with fcc phase on the end surfaces of the “arms”. The built in anisotropic feature of this materials enables to show superior electrocatalytic activity and stability toward HER under alkaline conditions compared to the commercial Pt/C and other reported electrocatalysts [91].

The heterostructure matrix with different phase enables in tuning the electronic structures and thus, establish the electrochemical activity for enhanched HER performance. Great efforts have made so far by fabricating 1T-MoS2 catalysts along with other phase(s) on supported catalysts to increase the catalytic active sites and stability as well. Developing an effective HER electrocatalyst hybrids with such phase(s) should establish balance between the good conductivity and rich active sites, which significantly boost up the HER rate for its practical application. Optimization to achieve such electrocatalysts for HER, we often see them make a coupling with graphene or carbon nanotube or dope with other compounds to give preferred structural properties, for example, high specific surface area and electrical conductivity; and synergistic electrical effects. Red phosphorous exhibits the ability to expand the interspace between S-Mo-S layers of 2H MoS2 bulk, which could further exfoliate the bulk MoS2 into thin flakes. Not only red phosphorous embeds into the S-Mo-S atomic plane but also induces the glide of S atomic planes around the P doping areas, allowing in-plane heterostructures originating from 2H and 1T MoS2 domains. Based on this assumption, Wang and workmates [43] have implemented one step annealing treatment methods following an ultrasonication process to fabricate and engineered such in-plane 1T–2H MoS2 heterostructures in order to evaluate the electrocatalytic HER performance. The resultant in-plane 1T–2H MoS2 heterostructures shows significant improvement in electrical conductivity, highly exposed active sites and long-time durability. Estimated electrical conductivity of 8620 Sm-1 was noted that is 500 times more than 2H-MoS2 (16.1 Sm-1) while its Tafel slope of 65 mV dec−1, high electrochemical surface active area of 60.3 cm2, hydrogen turnover frequency of 13.14 s-1 at 250 mV and 500 days stability performance at room temperature for HER in 1 m KOH electrolyte were reported. Additionally, they emphasized that the as-prepared in-plane 1T–2H MoS2 heterostructures may be act as potential electrocatalysts in an environment where simultaneous HER and OER can observe in one cell system. However, they proposed a different Volmer-Heyrovsky reaction mechanism for HER over the in-plane 1T–2H MoS2 heterostructures, rather than the conventional Volmer mechanism for 2H MoS2. There are couples of factors what actually responsible for this excellent activity, for example, more exposed active sites in the plane of 1T–2H MoS2 heterostructures than those at the basal plane of 2H MoS2; rapid electron transfer for accelerating HER activity due to the improved electrical conductivity; and the hydrophilic nature of the in-plane 1T–2H MoS2 heterostructures [43].

Application of 1T-MoS2 phase as co-catalysts with semiconductors can also spark the electrochemical activity of HER. To confirm such hypothesis, He [92] was attempted to fabricate the composite nanostructures along with metallic 1T-MoS2 phase with most frequent TiO2 nanotubes semiconductors and Si-doped TiO2 nanotubes, which hence showing an excellent electrochemical activity for HER. Unlike chemically exfoliated in-plane multiphasic MoS2 electrocatalysts which show Tafel slope of 43 mV dec-1, the 1T-MoS2 phase/TiO2 nanotubes heterojunction was subjected to Tafel slope of 42 mV dec-1. Yet the 1T-MoS2 phase addition on the Si-doped TiO2 nanotubes disclose a relatively low Tafel slope of 42 mVdec-1, indicating that this designed heterojunction may be able to provide good performance in the context of HER activity. Optimization of rich active sites along with conductivity could be a promising option to improve the HER activity. On this observation, Shi and co-workers [93] have fabricated 1T-2H-MoS2 phase nanosheets on carbon by incorporating 1T-phase in primitive 2H-MoS2 nanosheets via two step hydrothermal methods. Electrochemical experimentation shows that the composite materials have excellent electrochemical activity over primitive 2H phase. The calculated overpotential of 64 mV in 0.5 M H2SO4 at10 mAcm-2 and Tafel slope of 49 mV dec-1 reported, which surpassed by far the activity of previous MoS2 catalysts. The utterly and complete HER activity as well as good stability of the composites nanosheets materials is plausible, even likely because the alteration of electronic structure. For such good performance, the reasons were outlined that the abundance of unsaturated sulphur atoms from distorted structure, which works as active sites for HER, and the extent of disorder gives a quasi-periodic nanodomains arrangements that partially remains the 2D electron heterojunction, resulting in rapid interdomain electron transport. It is also assuming that the incorporation of the metal 1T phase in the primitive 2H-MoS2 matrix increases the intrinsic conductivity of the nanodomains and accelerates the conjugation between the positive protons and catalysts. Likewise, Liu and colleagues [94] have prepared 1T/2H-MoS2 polymorph via a facile one-step hydrothermal route utilizing thiourea and sodium molybdate dehydrate as the precursors for four hours at 180 °C with the assistance of propionic acid. The as-synthesized electrocatalysts show reasonable activities wherein overpotential and Tafel slope were about 220 mV at 10 mAcm-2 and 61 mVdec-1, respectively. The evaluated electrocatalytic performance is relatively lower as compared to those for exfoliated MoS2, while its preparation protocols could be applied for other TMD based materials with improved HER activity.

The formation of 1T MoSe2 nanosheets and NiSe nanowire arrays heterostructure could be able to improve the HER efficiency in a basic medium. Number of potential advantages could emerge from such heterostructure such as: (a) the 1T phase MoSe2 does the intrinsic catalytic activity and NiSe can promote water dissociation while merging these two features can results higher HER activity; (b) multidimensional activities like accelerating electron transfer along the axial dimension, efficient mass transport through solid-liquid-gas three-phase interfaces and easy gas escaping to release active sites can be done with NiSe nanowire cores; and (c) 1T‐MoSe2/NiSe nanosheet/nanowire (NS/NW) arrays supply available accessible active reaction sites at three-phase interfaces. Benefitting from such features, Zhang and co-workers [106] have prepared 1T‐MoSe2/NiSe nanosheet/nanowire (NS/NW) arrays for electrochemical water splitting and found that the in-situ electron injection from NiSe to MoSe2 induces the phase transition from 2H‐ to metallic 1T‐phase. With such heterostructure, a low overpotential of 200 mV at current density of 50 mA cm−2 was achieved along with excellent durability in basic environment.

An active electrocatalysts haven’t ever been shown true potential yet for ORR-a well-known reaction scheme, which reported to be associated with sluggish kinetics that requires four-electron transfer mechanism, however, a much more complicated process than HER. In acidic conditions, the four-electron process reduces O2 directly in H2O or OH- in basic solution (see below). The four-electron process can proceed through multistep mechanisms. Depending on the oxygen dissociation energy barrier on the catalysts surface, either a dissociative or associative mechanism has been suggested for direct four electron pathway [107]. Apart from direct mechanism, a two-electron transfer step leads to hydrogen peroxide formation first, followed by further reduction to water gives so called indirect mechanism [107]. Involvement of varied intermediates is the main distinguishing filter between these two mechanisms, which changes the framework of the free energy pathway.

The thermodynamic free energies of all the above intermediates were determined for a variety of close-packed metal surfaces and a volcano framework was designed relating the theoretical ORR activity and their oxygen binding energy, where Pt near the volcano peak as we have seen in Figure 3 [23]. If metal bind oxygen too strongly, then that ORR activity is subjected to the proton-electron transfer to either O\* or OH\*, while binding is too weak, then ORR activity is limited by proton-electron transfer to O2\* or splitting the O-O bond in O2, depending on the applied potential [23]. The former one is the associative mechanism while the later one is dissociative mechanism. However, the benchmarking ORR catalyst is Pt in terms of efficiency but their scarcity and stability issues (Pt agglomeration, dissolution, sintering, detachment, and corrosion of carbon support materials) nullifying their potential application. In an attempt to alleviate this problem, many studies have been done towards the rational design and fabrication of a novel ORR electrocatalysts with activity comparable or even superior to that Pt based electrocatalysts [108, 109]. Very recently, it was realized that phase-based electrocatalytic materials such as MoS2, WS2 and TaS2 have potency in improving the ORR activity. Among them, the layered TaS2 material show three basic phases namely 2H, 1T, and 3R, while suitable synthetic methods generate only 2H and 1T phase because 3R generally have a mixture of other phases [108]. The idea of 1T-MoS2 application in HER motivates the usage of different phases of TaS2 in ORR as well for HER since the phase transformation can change the catalytic activity. Both of 1T-TaS2 and 2H-TaS2 phases show comparable catalytic performance to that of Pt/C catalysts, which can be increased further upon electrochemical pre-treatment indeed. The authors stated that the presence of Ta2O5 oxide during the oxidation may accelerate the activity of 2H-TaS2 phase. Computational results indicate that the free energy of hydrogen adsorption on basal planes and edge sites of each phase has significant effects on respective reactions [108]. For example, the binding energy of hydrogen atoms on edges is too weak for 1T-TaS2 phase, which led to positive values for ∆G over the whole hydrogen coverage range (Figure 6). At 25% coverage, the value close to thermoneutral (∆G = 0.46 eV) was observed. At higher coverage, hydrogen adsorption became even less favourable, which results in poor HER performances. Other than this, the HER activity remains less active on basal plane since it binds hydrogen atoms very weakly (∆G = 1.24 eV) [108].

In order to improve the ORR, a new class of heterostructured (La,Sr)2FeO4−δ (LSF214)-La0.8Sr0.2FeO3−δ (LSF113) electrode materials have emerged, which consists of a Ruddlesden–Popper (R–P) LSF214 phase formed on the surface of the LSF113 framework [110]. The higher catalytic activity of the LSF214 phase and the lattice mismatch between the LSF214 and LSF113 interfaces accelerates the oxygen vacancy formation and oxygen molecule adsorption, resulting in one order of magnitude improvement in ORR activity.

In what is a win–win situation for electrocatalytic HER over the phase-based materials, the much less is realized for OER because the sluggish kinetics and required high positive potential to compensate the kinetic barrier [23]. It is important to keep in mind that oxygen reduction reaction (ORR) is another slow kinetics and overpotential phenomena in electrochemical studies. An active OER catalysts in acidic medium, have reasonable binding energies to couple with intermediates [23]. In terms of activity and stability, the OER catalysts, however, need to be shown with superior performance under respective reaction conditions, especially under high oxidative potentials. While we have seen much efforts in the rational design and modulation of HER electrocatalysts, the less concerns have been paid in the developing an OER electrocatalysts, which is the major bottleneck of electrochemical water splitting [23]. It is highly desirable that as long as the HER activity realize over an electrocatalysts, the efficient overall water splitting also requires high OER characteristics for electrocatalysts under the identical operating condition. As far as we have seen from literature survey that the Volmer reaction associated with water splitting under alkaline solution includes the water dissociation step at the beginning of the HER, making the overall process troublesome while in acidic environment such dissociation is relatively understood [111, 112].

The MoS2 and TaS2 have been studied for HER for many years while just recently the electrocatalytic activity for OER was revealed over these two materials [113]. The reaction scheme for OER needs four electron proton transfer process with the intermediates like OH\*, O\*, and OOH\*-a similar mechanism on the catalysts surface that happens for metal oxides, nitrides, sulphides (Figure 7) [113]. Computational guidance shows that the edges sites of both MoS2 and TaS2 are more active than their basal plane sites in the context of OER performance. In plotting free-energy diagram for evaluating the activity of edge sites in acidic solution, it verifies that the 1T phase edges have least kinetic energy barrier and the 2H phase is the most active one with 50% sulphur coverage. For most of the phases, the OER activity is limited by splitting water with one proton-electron transfer process (O\* + H2O → \*OOH + H+ + e−), which introduces the overpotential needed to overcome the barrier of O=O formation [23]. The oxygen formation step via (OOH\* → \* + O2 + H+ + e−) has the largest free-energy difference that occurs with S‐edge sites of 2H‐TaS2. With highest content of 1T phase, the as-prepared polytype reached a Tafel slope of 46 mV dec-1, inferring that the multiphasic 1T/2H-MoS2 nanostructures pave the way for improved electrocatalytic performance. The plotted volcanoes indicates that the activity of edges of 1T‐MoS2 and TaS2 is comparable with that IrO2 and manganese oxides (Figure 7) [113]. The experimental investigation has revealed that an overpotential of 0.42 V need to reach the current density of 10 mAcm−2 with 1T‐MoS2 phase, demonstrating most efficient catalytic activity among others (0.45, 0.48, and 0.54 V for 1T‐TaS2, 2H‐MoS2, and 2H‐TaS2, respectively). While this activity is comparable with some electrocatalysts, for example, Mn oxide (0.54 V), and Mn3O4/CoSe2 (0.45 V) in alkaline solution, but a little worse than IrOx electrocatalysts in acidic solution [113]. Tafel plots show relatively high values of approximately 322, 282, 361, and 255 mVdec−1 for 1T MoS2, 1T TaS2, 2H MoS2, and 2H TaS2, respectively. However, with annealing treatment, the phase turns into reverse direction from 1T‐MoS2 to 2H‐MoS2 resulting in decrease in catalytic activity-a confirmed approach that is in acidic solution, the 1T phase exhibits higher catalytic activity toward water oxidation than that of 2H phase [113].

With various crystal phases, the noble metal core-shell nanoparticles could be an excellent choice for EC-OER because the synergistic effects between the multicomponents, unusual crystal structure and core can increase the electron transport at the interface. Based on that idea, Fan and colleagues [114] have prepared 4H/ fcc -Au@Ir core-shell NRBs and evaluate their performances for EC-OER. It was highlighted that the Tafel slope was about 51.4 mV/dec, which was lower than that of the commercial Ir/C catalyst (74.3 Mv/ decade), inferring the highly efficient oxygen evolution activities of Au@Ir NRBs. The plausible reasons were the accelerate electron transport due to the 1D Au core in Au@Ir NRBs, the abundance of the active sites in the dentritic structure and the synergistic effects between the different components that is Au and Ir [114].

Electrocatalytic overall water splitting reaction has been recognized promising in producing both hydrogen and oxygen in presence of an active catalysts. It is important in this reaction that the catalytic materials should have the ability to suppress the HER and OER activity regardless of the reaction medium. This is likely that the water dissociation related Volmer steps is stemmed from an unfavourable orbital orientation of the employed catalysts. It is thus necessary to synthesize the catalytic materials with various crystal phase that can ameliorate the kinetic barrier. In the following section, we will examine and discuss some phase materials from the recent published papers.

As part of the growing scientific advancement in energy conversion processes, the water splitting in presence of electrocatalysts appears to be promising approach in producing hydrogen fuels -a functional and practical means [115, 116]. The main obstacle in achieving high performance from water splitting is lowering the driving overpotential and improved efficacy of that electrocatalysts. The expected performance over electrocatalysts for overall water splitting system is largely dependent on (a) intrinsic activity of catalytic active sites [117], (b) improved conductivity of the electrode material [118], (c) increased mass transfer properties, and (d) elevated density of electrocatalytic active sites or improved surface area of the electrocatalysts [119].

Li and colleagues [120] have studied the overall water splitting system to evaluate the hybrid nanotube arrays (FeCoNi-HNTAs) performance for OER and HER reactions, respectively. Due to its excellent electrode kinetics, facile charge transfer, and improved intrinsic electrocatalytic HER activity, the 1Tʹ-MoS2 was incorporated within that hybrid nanotube arrays. The FeCoNi-HNTAs was prepared from ternary Fe, Co, Ni-based layered double hydroxide nanowire arrays (FeCoNi-LDH-NWAs) supported on Ni foam substrate. The FeCoNi-HNTAs display striking performance for HER and OER reactions in terms of catalytic activity and durability. Results show that an overpotential of 58 mV and 184 mV was realized at current density of 10 mA cm−2 for HER and OER reactions, respectively, whereas an extraordinary durability of 200 mA cm−2 for 80-h continuous operation was noticed. The reported Tafel slopes for HER and OER were 37.5 mVdec−1 and 49.9 mVdec−1 respectively, elucidating the rapid reaction dynamics. The overall cell voltage of 1.429 V in alkaline electrolyte solution was monitored at current density of 10 mAcm−2 when the FeCoNi-HNTAs was employed both as anode and cathode simultaneously for overall water splitting (Figure 8).

The plausible reasons for that hybrid structure are ascribed to the 1Tʹ-MoS2 activities and synergistic role of trimetallic system. During OER reactions, Fe3+ works as highly active electrocatalytic sites for OER since the intermediate species can easily adsorb on the Fe sites due to the lower Gibbs free energy. In addition, it is proven that addition of Fe could lower the overpotentials and increase the catalytic activity of Ni-based compounds for OER reactions. The contribution of Co ions is to adjust the electronic state of Fe and give high valence state, while the Co3+ ions position at octahedral sites are beneficial for OER than that of Co2+ ions position at tetrahedral sites, which improve the intrinsic activity for OER reactions. The incorporation of Fe and Co with that of Ni-based compounds is seen to be as captivating promoter because the increase of Ni3+ quantity effect on the local electronic configuration and hence, increased the electrocatalytic performance as well [120]. On other side, the 1Tʹ-MoS2 phase was able to keep its metallic 1Tʹ-MoS2 phase under both OER and HER operation, signalling that the stability of 1Tʹ-MoS2 phase was significant at both oxidation and reduction potentials. It is possible that the 1Tʹ-MoS2 phase could return in its semiconducting 2H phase under the influence of reactions conditions, such as temperature, however, in this case it was not. However, the long-term OER operations can oxidized the MoS2 indicating that 1Tʹ-MoS2 could impact on both half reactions of water splitting [120].

In their previous studies [121], they have evaluated porous hybrid nanostructures together with amorphous Ni-Co complexes with 1T phase MoS2 (referred as PHNCMs) as function of hydrazine (N2H4) quantity for overall water splitting reaction. Ni-Co hydroxides ultrathin nanosheets (NCUNs) act as the precursors and templates for the subsequent PHNCMs synthesis. They highlighted that an overpotentials of 70 mV and 235 mV were achieved at 10 mAcm−2 for HER and OER respectively, over the hydrazine-induced PHNCMs electrocatalysts, demonstrating the highly active and ultra-stable electrocatalytic performances [121]. The calculated Tafel slope values indicate the rapid reaction rate mechanisms for HER (38.1 mVdec−1) and OER (45.7 mVdec−1). In terms of overall water splitting efficiency, they reported an overvoltage of 1.44 V in achieving current density of 10 mAcm−2 for 48 h operation without degradation (Figure 9). The possible reasons for that performances over PHNCMs was subjected to the amount of hydrazine hydrate (HZH), which was responsible for the phase transformation of MoS2 and the crystallization of Ni-Co-based compounds [121]. As with HZH, Ni-Co-based compounds were changed from partial metallic state into amorphous complexes and MoS2 is transformed into metallic 1T phase. The electron-donor ability of HZH could increase the amorphous Ni-Co complexes, which further stabilize the 1T phase MoS2. The facile electrode kinetics, improved electric conductivity and skyrocket electrocatalytic active sites, can be realized with that of 1T phase MoS2. They have also been elucidating that the porous nanostructures have potency to generate more active sites and can increase the mass transport and gas permeability successfully during water electrolysis. In addition, the preferential intramolecular proton transfer ability of the hydrazine-induced Ni-Co complexes is thought to be advantageous in reducing the overpotential of electrocatalytic H2 evolution [121]. Therefore, the PHNCMs nanostructures have augmentative capacity in increasing the electrocatalytic performance for overall water splitting.

A good understanding on how that metallic MoS2 phase affects the overall water splitting reactions, especially on the OER and HER is of great importance. The engineering and architecting of heterointerfaces along with metallic MoS2 have some beneficiary effects for overall water splitting reactions. Zhang and co-workers [122] have designed multiples heterointerfaces along with metallic MoS2 and evaluated how these heterostuctures facilate the intrinsic activities of the electrocatalysts. In basic medium, the water undergoes dissociation (Volmer step), produces intermediates H\* and OH- those needs to be chemisorbed on the surface of HER assisted electrocatalysts [17]. If an electrocatalysts can do that task effectively, an improved performance can be realized at the end. Likewise, the water-oxidation activities for OER in basic medium depends on the chemisorption and dissociation of OH- and the produced reaction intermediates such as OH\*, OOH\*, and H+ [123]. So, the OER electrocatalysts that have ability to combine both chemisorbing oxygen containing and hydrogen intermediates at a time, can increase the water-oxidation reaction. There are reports that the undercoordinated Mo-S sites along the edges of MoS2 shows high chemisorption ability for both OH- and oxygen-containing yields, therefore, enhancing the overall electrochemical water-splitting performance [104]. For example, a favourable HER performance was realized for the interfaces between MoS2 and Ni3S2 while the heterointerfaces between MoS2 and NiO favour the OER process [122]. Density functional theory (DFT) analyses reveal that the chemisorption free energy of H is -3.17 eV on the surface of Ni-doped MoS2 (Ni-MoS2 samples), which is much lower than those (101) surface of Ni3S2 ( -1.81 eV) and (002) surface of MoS2 (-2.71 eV), indicating that H chemisorbed preferentially on the Mo-S edge sites (Figure 9) [122]. On opposite sides, the chemisorption free energy of HO is -2.92 eV which is lower than those on surface of MoS2 (-1.68 eV) and surface of Ni3S2 (-2.36 eV), signalling that the surface undercoordinate Ni sites of Mo-doped Ni3S2 (Mo- Ni3S2) is the first choice for HO chemisorption. The oxygen containing intermediates show strong binding ability towards on (101) surface of Mo-Ni3S2. In addition, the chemisorption free energy of HO on the interfaces between MoS2 and NiO for OER is -5.12 eV, inferring that the Mo sites of Mo doped NiO (Mo-NiO) affords the process easily. According to the DFT evaluation, it is concluded that both Mo-Ni3S2 and MoS2-NiO interfaces affords the H-chemisorption of MoS2 and HO-chemisorption of Ni3S2 and NiO. By adopting such intrinsic capacity, an ideal electrocatalysts can improve the overall water splitting reactions, through the deployment of HER and OER processes effectively [122].

Photocatalytic and photoelectrocatalytic water splitting are recognized as two of the most promising approaches in producing hydrogen utilizing the solar energy. Since both processes takes place under light illumination, therefore, the employed catalytic materials in these redox processes should fulfil some physical requirements. The band position and band gap are the two key requirements in water splitting photocatalysis while the catalytic materials should have a minimum bandgap of 1.23 eV to meet the redox potentials of the H+/H2 and O2/H2O pairs. However, a plethora of the photocatalytic materials have been evaluated in these redox reactions, while there are numbers of phase materials also gained consideration. The SPE could be effective in these redox processes since it can allow to achieve the tuneable band gap of the materials as well as other electronic properties what we will see in the following section.

A keen interest accumulates among the scientific community to produce clean hydrogen fuel from so-called photocatalytic water splitting reaction through utilizing HER reactions over the earth abundant semiconductors because this is the most prominent way to convert solar energy into chemical products. Application of many novel photocatalysts have been theoretically and experimentally investigated for HER that includes metal oxides [124, 125], silicides [126], carbides [127] and chalcogenides [128]. The application window of these photocatalytic materials, however, needs to be identified in detail because photon-to-exciton conversion, charge carrier (e-/h+) recombination, light-adsorption range, quantum efficiency, etc; which is more likely related with their nanostructural properties [129]. Adding co-catalytic materials on semiconductor surface could improve the photocatalytic activities, providing more hydrogen reduction sites, and reduce the activation energy that ultimately accelerate the proton reduction [130, 131]. In this regard, owing to having large surface to volume ratio, tunable bandgap, suitable band position, and highly active chalcogenides atoms at the exposed edges makes TMDs materials and some other metal oxides an unparalleled candidate for photocatalytic HER [1, 132]. To improve the photocatalytic activity, attention has been given on synthesizing cheaper photocatalytic materials rather than noble metals. As part of this advancement, the study of reaction mechanism of hydrogen evolution activity has also done [133]. However, at the end of this section, we provide a summarized overview (Table 2) of the recent publications that uses photocatalytic concept for hydrogen production.

The phase engineering approach marks a crucial step towards finding the latent potential of 2D TMDs materials, which is indeed a provoking progress that could be a solution for many problems in materials science fields. Cho and co-workers [29] have observed that based on stacking geometry, MoS2 shows two polymorphisms namely 2H and 1T phases. By twisting one set of the 2H Mo-S tetrahedron by a 60° rotation, one can achieve 1T phase. The 1T phase is metastable in nature while 2H phase is stable and has a semiconductive character. To stabilize the 1T phase, one has to be pumped electrons into it which in turns, become metallic in nature due to the half-filled d-orbital band. Introduction of distortions and/or defects in the structure of TMDs material fetch different properties, for instance, the 1T-MoS2 displays conductivity by a factor of 107 higher than its counterpart 2H phase. Maitra and colleagues [134] have demonstrated that the hydrogen evolution activity of single layered 1T-MoS2 photocatalysts is higher than nitrogen doped graphene 2H- MoS2. This is likely to happen that reduced graphene as an electron transporter to MoS2 increases the metallic conductivity of MoS2 itself. The HER activity over single-layered 1T-MoS2 photocatalysts suggested the formation of a p-n junction in composites of n-type N-doped graphene with p-type MoS2. It is worth to note that the overall reaction scheme is about the photocatalytic generation of hydrogen, the electron involved in the reduction process does not photocatalytically formed on MoS2 surface while transferred from photogenerated species Eosin (EY-) to MoS2. Additionally, Xu and colleagues [11] have designed the metallic 1T-MoS2 phase as co-catalysts on 2D oxygenated g-C3N4 semiconductors using the in-situ growth method for PC-HER activity. Amongst the prepared photocatalysts, the 1T-MoS2/O-g-C3N4 shows outstanding photocatalytic performance wherein the highest H2 evolution rate was reported about 1841.72 μmol g-1h-1 for optimum 1T-MoS2 loadings. At λ = 420 nm, the external quantum efficiency of 0.2% 1T-MoS2/O-g-C3N4 2D heterostructure was about 7.11% which is the highest value in all g-C3N4-based systems using Pt-free co-catalysts. For such outstanding photocatalytic performance, the possible reasons were outlined that the exposed edges and basal plane could be catalytically active for both photocatalysts while reduced contact layer between 1T MoS2 phase and O-g-C3N4 semiconductors facilitates the photo-induced electrons transfer from conduction band to the 1T MoS2 phase, which therefore, in turn, accelerates the electrons participation in PC-HER. Moreover, the designed 2D heterostructure junction of 2D semiconductors supported 2D metals through van der Waals interaction minimizes the Schottky barrier or even wipes out the schottky barrier because of weak Fermi level pinning which is an important factor for improving charge transfer on the surface.

Nevertheless, Zeng and colleagues [7] have identified that an effective photocatalytic HER might be achieved through the structuring and engineering the phase junction between triazine-based crystalline carbon nitride (tri-C3N4) and tri-s-traizine-based crystalline carbon nitride (tri-s-tri-C3N4). Actually, the tri-C3N4 composite vertically aligned on the surface of tri-s-tri-C3N4, which is crucial for gaining higher photocatalytic H2 evolution activity of 144 μmol/h that is 30 times higher as compared to pristine g-C3N4. The reason is the formation of crystalline tight junction between these two composites, which significantly boost the transfer and separation efficiency of the photocatalytic charge carriers. Because of this tuned property, more charge carrier can diffuse larger path on the junction area for directional separation. Besides, Yi and colleagues [135] have experimented metallic 1T-WS2 phase as a co-catalyst on 2D graphitic carbide nitride (g-C3N4) using a facile solvothermal approach for improving the photocatalytic hydrogen evolution. As expected, the composite materials show an impressive performance as compared with the bare 2D-C3N4 and 2H-WS2/2D-C3N4 photocatalysts. The documented reasons were the excellent electrical conductivity through the designed p-n junction and improved active sites on the basal plane rather than exposed edge sites of the fabricated photocatalysts. They engineered the 1T-WS2 phase into 2H-WS2 phase via thermal annealing treatment route wherein its performance remains questionable. Phase conversion of 1T-WS2 phase (64.1% concentration of 1T phase) at 400 °C shows higher H2 evolution rate of about 331.09 μmol g−1h−1, which is almost 43.3- and 1.94-folds increment as compared with the bare 2D-C3N4 and 2H-WS2/2D-C3N4 photocatalysts. The 1T phase concentration decreases from 64.1% to 48.7% and 25.7% as with the annealing temperatures decreases from 400 °C, 300 °C to 200 °C while H2 evolution rate also reduces 331.09 μmol g−1h−1 to 208.69 μmol g−1h−1 and 171.51 μmol g−1h−1. This photocatalyst provides external quantum efficiency of about 1.12% at 420 nm wavelength indicating that 1T-WS2 phase can accelerate the charge transfer to the surface and able to reduce the overpotential barrier for reactions happening.

Because of its distinctive phase‐engineering nature, the MoS2 materials show excellent stability and high efficiency for hydrogen evolution. Liu and colleagues [136] have investigated the hydrogen evolution over metallic 1T-MoS2 hybrids at gram-scale using hydrothermal synthetic pathway. The structural phase transition occurs from 2H‐MoS2 into 1T‐MoS2 with deployment of electron donation from NH4+ ions while the application of alkali metals for this purpose was deliberately avoided. The elucidate reason is the long-term stability of 1T‐MoS2 phase because Li+‐intercalated products show limited stability. Coupled with CdS nanorods semiconductor, the fabricated nanocomposites unfold highest hydrogen yield of 9.11 mmol g−1h−1 at 300 W Xe light source than that of pristine CdS nanorods and 2H‐MoS2/CdS nanocomposites those gives 440 µmol g−1h−1 and 3.07 mmol g−1h−1, respectively. Interestingly, the 1T‐MoS2/CdS nanocomposite display prolonged durability even after five reused cycles. The prime argument for such PC-HER performance over 1T‐MoS2/CdS nanocomposite is the rapid charge-transfer ability. However, according to theoretical assumptions, they indicated that the metallic nitrogen doped MoS2 structure could be more effective for improved hydrogen activity as cocatalysts rather than chosen semiconductors because such doping could speed up the electron-hole separation efficiency and create more active sites. In their complementary works, the 1T‐MoS2/CdS nanocomposite prepared from a facile one-step solvothermal approach. The maximum hydrogen generation rate of 17.479 mmol g−1h−1 over an optimum loading of 0.2 wt% 1T‐MoS2 on CdS semiconductor, which yet a 39-fold higher increment in terms of photocatalytic activity as compared with pristine CdS nanorods. What is significantly striking here in increasing photocatalytic performance of CdS nanorods semiconductor that the synergistic effects root from the intimate heterojunctions between the interfaces and rapid electron transport in the metallic phase of 1T‐MoS2 [137].

Du and associates [53] have synthesize the 1T-MoS2/CdS NRs and 2H-MoS2/CdS NRs hybrids with various phases of the MoS2 nanosheets using hydrothermal methods. With 10 wt% 1T‐MoS2/CdS nanorods heterojunction, the hydrogen generation rate of 794.93 µmol g−1h−1, which however, approximately 35 times and 4.5 times higher than that of pristine CdS nanorods (22.51 µmol g−1h−1) and 2H‐MoS2/CdS nanorods (175.82 µmol g−1h−1), respectively. Despite that, the loading more than 10 wt% 1T‐MoS2 nanosheets might be deleterious because the photocatalytic performance decreases gradually over the CdS nanorods along with light shielding by MoS2. Evaluation on photocatalytic durability reveals that the addition of 1T-MoS2 and 2H-MoS2 have the potency to alleviate the photocorrosion even after 12 hours light irradiation. However, the reaction mechanism explains from the fact that the interface between 1T‐MoS2 and CdS easily forms an Ohmic contact, which is able to reduce the contact resistance and accelerate steady photoexcited electron transfer, and therefore, 1T‐MoS2 could be considered as an excellent facilitating cocatalyst for the CdS photocatalyst.

Wu and associates [138] have engineered different phases of MoS2 sample on g-C3N4 semiconductor in accelerating the electron-hole pair separation and boost up the hydrogen evolution rate. A 0.2 wt% 1T-MoS2/g-C3N4 nanojunctions discloses highest hydrogen evolution rate of 948.7 µmol g−1h−1, which is almost 26 times and 83 times higher than those of 2H-MoS2 phase and pristine g-C3N4 , respectively, at same experimental conditions. It could be possible that the g-C3N4 possess highly defined and unambiguous structure with minimal thickness, large aspect ratios, homogeneous tri-s-triazine-based units, and high crystallinity [139]. However, the combination of 1T-MoS2 and g-C3N4 could be a feasible photocatalysts for hydrogen evolution because of its rapid charge pair separation and the composites itself does not decay under controlled experimental conditions. Making nanocomposites junction between 1T-MoS2 and other compounds may uncover true intrinsic performance of the photocatalysts for HER. Believing that speculation, Liu and workmates [140] have prepared 1T polymorph of MoS2 on Zinc Indium Sulfide (ZnIn2S4) surfaces by means of lithium intercalation using hydrothermal methods. Due to presence of lithium ions, the MoS2 samples change its phase structure from 2H to 1T. The photocatalytic activity is subjected to the quantity of engineered 1T-MoS2 phase in the composites. A 2.0 wt% 1T-MoS2/ZnIn2S4 composites exhibits higher hydrogen formation rate of 332.4 μmol h−1, which 2.4 and 1.3 times higher than those bare ZnIn2S4 and 2.0 wt% 2H-MoS2/ZnIn2S4 composites, respectively. This is more likely that the photoinduced electron-hole pair on ZnIn2S4 surfaces can easily isolated in presence of 1T-MoS2 phase because of its increase electrical conductivity and high volumetric active sites.

Integration of 2H-/1Tʹ-MoS2/graphene photocatalysts in both lateral and vertical direction by means of super critical carbon dioxide treatment proves an excellent performance rate for hydrogen evolution where note that graphene works as electron acceptor and transporter in the heterostructures. Band position between the two MoS2 phases were at good that promotes shifting of the electrons from 1T′-MoS2 phase to the 2H-MoS2 phase to fill the photoinduced photoholes via the lateral heterojunction structure, which in turn, reduce the recombination process between the charge carriers as shown in Figure 10. It is worth to note that a higher photocurrent density for HER was marked [141]. However, the reported synthesis protocols are questionable because it is elusive that how exactly this heterostructure fabricated to ensure graphene selectively heterointerfaced with 1T′-, not 2H-MoS2, as designed needs to be further investigated. In a separate study, Chou and workmates [51] have evaluated the structural exfoliation of MoS2 by means of lithium intercalation and demonstrated that how the varying physical structure can impact on the HER photocatalysis.

Computational studies reveal that with increasing lithiation, the Mo atoms of MoS2 became asymmetrically spaced, resulting in generating 1T′ phase, which promotes the normally inactive basal plane prone to hydrogen adsorption and hydrogen evolution. Additionally, the monolayer exfoliation enhances the surface area by as much as 1000-times, which is beneficial because the basal plane activation gives non-trivial enhancement in catalytic performance as compared with exposed edge sites dominated catalysis of 2H-MoS2 phase. Such powering strategy over MoS2 samples display 4-fold increase in hydrogen yield [141].

The 2H-MoS2 phase is a semiconductor with narrow band gap, i.e. 2 eV, while metastable metallic 1T-MoS2 and quasi-metallic 1T′-MoS2 show higher electric conductivity. Yet the 2H-MoS2 phase regards as photocatalysts but its slow electron transfer in the MoS2 plane makes them unfeasible from wider application because such activities encourage the electron-hole pair recombination and thus reduce the photocatalytic activity. Chang and co-workers [45] have prepared different phase based MoS2 samples using lithium molten salt intercalation at different temperatures. They performed the photocatalytic hydrogen evolution over these samples and reported that hydrogen yield of 1563.6 µmol g−1h−1 at the corresponding apparent quantum efficiency of 24.1% at 420 nm was achieved on 1T-MoS2 phase while its 2H-MoS2 provides approximately 1658.5 µmol g−1h−1 of hydrogen as shown in Figure. The higher photocatalytic activity of 2H-MoS2 samples on CdS semiconductor linked to its smaller particle size as compared with 1T-MoS2 phase. Additionally, they differentiate the photocatalytic activity in the context of CdS and TiO2 semiconductors band matching with that MoS2 samples. Because of quantum confinement effect, the monolayer 2H-MoS2 samples have larger bandgap (1.3 eV) than its bulk MoS2, where its conduction band (CB) minimum position is more negative than that of TiO2. From theoretical perspective, it might be improbable that the photoinduced electron from TiO2 can go into the CB of 2H- MoS2 samples for hydrogen reduction. Conversely, the photo-excited electrons can easily inject into both 1T and 2H-MoS2 for hydrogen evolution reaction due to the more negative CB position of CdS as shown in Figure 11.

To improve the photocatalysis, it necessitates to fabricate intraplane heterojunction because the different phases of MoS2 exhibit diverse physical and chemical properties. Literature survey indicates that with possible designing and fabricating the 1T/1T′ phase MoS2 along with 2H-MoS2 phase in the same plane, might be beneficial for reducing charge recombination process because the rapid photogenerated electrons and holes can transfer from 2H-MoS2 phase to 1T/1T′ phase MoS2. Based on that ideas, the multiphasic single-layer MoS2 was developed and found that it works well thanked to the 2H- MoS2 phase which absorbs the visible light and create charge pairs while photoinduced charge pair separated via intimate contact between the 1T/1T′ phase MoS2 and 2H-MoS2 phase [142]. More specifically, at the interface of n-type semiconducting 2H-MoS2 and 1Tʹ-MoS2 phase formed an upward band-bending Schottky barrier, through which photogenerated electrons flowed from 2H-MoS2 to 1Tʹ-MoS2. The hydrogen evolution reaction happens on both basal and edge sites of 1T′-MoS2 phase along with edge sites of 2H-MoS2 phase, resulting in four times higher hydrogen evolution rate as compare with pure 2H-MoS2 phase. The designed heterostructure interface between 1T′-MoS2 phase and 2H-MoS2 phase is shown in the Figure 12.

The phase engineering of nano and microcrystalline photocatalysts in terms of their physical and optical properties could be an emerging approached enabling highly effective water splitting for hydrogen generation. It is worth to note that the various crystallographic and electronic structures resulting in distinct effective masses of photogenerated carriers, mobility of them, and electron-hole pair togetherness, etc; leading to different photocatalytic performances of dissimilar phases. Relationship studies between crystal structure and electronic structure is crucial because crystallographic symmetry have great influence on photogenerated charge carrier excitation and thansfer them to the catalytic surface. In photocatalysis, NaNbO3 is known as highly stable and multi phase perovskite which was proven to be a competitive candidate for hydrogen generation under light irradiation. Li and co-workers [143] have prepared cubic NaNbO3 phase (c-NaNbO3) and orthorhombic NaNbO3 phase (o-NaNbO3) to understand the synergistic relationship between their electronic structure and photocatalytic properties. Hydrogen evolution were calculated approximately 127 and 72.3 μmol h−1, respectively, for c-NaNbO3 phase and o-NaNbO3 phase under 300 W Xe lamp at λ > 300 nm. Possible reasons ascribe to their different electronic structures. In parallel works, Zhang and associates [66] have studied the photoreactivity of temperature dependent crystalline phases such as cubic KNbO3 (c-KNbO3), othrorhombic KNbO3 (o-KNbO3), and tetragonal KNbO3 (t- KNbO3) from aqueous methanol under UV. With small amount of Pt cocatalysts, the c- KNbO3 phase provides approximately 1242 μmol h−1g-1 of hydrogen at quantum efficiency of 1.95 % while a 333 μmol h−1g-1 of hydrogen at quantum efficiency of 0.53 % was reported for o-KNbO3 phase and a 118 μmol·h−1g-1 of hydrogen at quantum efficiency of 0.16 % was reported for t-KNbO3 phase. As is evidenced that the higher photocatalytic performance achieved with c-KNbO3 phase than those o-KNbO3 and t-KNbO3 phase because it has high number symmetry in the bulk structure and associated unique electronic structure. Beside that, the improvement in either the charge carrier lifetime or the electron-transfer rate constant at the interfaces caused the high quantum efficiency, which is perhaps regulated by the electronic structure of KNbO3 perovskites sample. A recent computational study [144] reveal that c-KNbO3 phase has largest electron mobility, smaller electron effective mass of photoinduced electrons, lower electron hole pair recombiantion rate and much better light absorption capacity than those of those o-KNbO3 and t-KNbO3 phases. Therefore, the photoreactivity of cubic phase should be higher than other phases. Similarly, Chang and colleagues [145] have investigated the multi-crystalline phases of Cu2ZnSnS4 (CZTS) chalcogenide semiconductors for hydrogen evolution under UV-vis irradiation. The wurtzite CZTS phase produces 21.2 μmol h−1g-1 of hydrogen while 54.8 μmol h−1g-1 of hydrogen belongs to kesterite CZTS phase, which is approximately 3-fold higher than wurtzite CZTS phase. The kesterite CZTS phase remains stable upto three cycles of 12 hours. It was clarified that the improved photocatalytic activity over CZTS is correlated with the band position of kesterite and wurtzite CZTS and the phase composition. The surface atomic configuration and different electronic structure (band structure) in different phases are responsible for enhanced photocatalytic performance. Both kesterite and wurtzite CZTS are in direct band gap in nature while the CB and VB of kesterite CZTS are more dispersive, signalling that it possesses lighter effective masses than that wurtzite CZTS phase [145]. As a result, the kesterite CZTS exhibited faster electron and hole migration abilities onto the surface. Additionally, the dominant exposed facets of kesterite CZTS is {112} facet which is polar and instable facets with alternate cation and anion layer. Such instability of the kesterite CZTS has increased its intensity to absorb the cations and/or the anions and that can leverage the charge imbalance. On other side, the wurtzite CZTS shows {100} sidewalls, which is a cation-anion parallel alignment surface. Overall, the kesterite CZTS shows phase dependent photocatalytic performance for H2 evolution. The structural phase materials can be used not only in promiting electron-hole speration during photocatalysis either by electron or hole trapping, but it can supply sufficient reactive catalytic sites for redox reactions. Application of structural phase materials as co-catalysts have significant influence on the photocatalytic performance since they can boost the interfacial charge transfer, thus facilitates the surface reactions as well. However, a proper band alignment between the co-catalysts and the light-harvesting materials is essential to obtain the maximum benefit from the interfacial charge transfer processes. To obtain such alignment, the engineering of the structural materials is needed at first. For example, the structured MoS2 and WS2 can be utilized as co-catalysts for improving the photocatalytic activity from water splitting reaction for hydrogen production. Bai and colleagues have prepared hybrid junction between TiO2 nanosheets and 1T-MoS2 nanosheets by means of lithium exfoliation using bulk MoS2. They achieved higher PC-HER activity over 1T-MoS2/TiO2 heterostructure than those 2H-MoS2. They signaled that the 1T-MoS2 phase increase the number of active sites on basal plane and edges for hydrogen evolution while its works as electron delivery channels. In 2H-MoS2 phase, the active sites located only in edges of nanosheets. On other side, the 1T-MoS2 phase adopts higher charge transport mobility and have higher density of the reactive sites that makes them an excellent candidate in photocatalytic H2 evolution as shown in Figure 13. Therefore, the loading of TiO2 nanocrystals onto 1T-MoS2 phase shorten the electron diffusion distance and increase the diffusion rate as compared with the loaded TiO2 over 2H-MoS2 phase. As a result, the 1T-MoS2/TiO2 heterostructure shows extended photocatalytic activity for H2 production than that of 2H-MoS2/TiO2 phase.

Mahler and co-workers [147] have engineered preparation protocols for making colloidal WS2 monolyers along with 2H phase or 1T′ phase. The as-prepared 1T-WS2 nanosheets doped by P25-TiO2 via simple adsorption method which enhance the hydrogen evolution rate by more than 3-fold to 2570 μmol g-1h-1 than those bare P25. In Figure 14 (a), shows that the 1T-WS2 possessed high work function, which play the key role in trapping the photon translocation of the electrons from TiO2 and boost the H2 production. The semiconducting 2H-WS2 phase work as light-harvesting material, which simultaneously provides the photoinduced electrons into TiO2 and supply recombination centers for photoinduced electrons and holes in the TiO2. The heterostructures with 2H-WS2, however, reduce the hydrogen evolution rate as shown in Figure 14 (b).

Similarly, the assistance of 1T-MoS2 as a co-catalyts reveals higher photocatalytic H2 activity when coupled with TiO2, while less performance was realized over 2H-MoS2 phase [45]. As opposed to this finding, it was reported that the photocatalytic performance in terms of H2 over 1T-MoS2 was much lower than that 2H-MoS2 phase, when they loaded with CdS materials. We hypothesise that the CB band position of CdS (band gap ~2.4 eV) was more negative than those for 2H-MoS2 (band gap ~1.85 eV) and 1T-MoS2 phase, which accelerates the electrons pump in 1T-MoS2 and 2H-MoS2 from CdS easily. In TiO2 case, the CB band position was lower than 2H-MoS2 phase, which is not feasible for an electron to move there, rather they shift in lower CB of 1T-MoS2 phase [45]. He and co-workers [148] have investigated the photocatalytic performance of silicon doped TiO2 nanotubes mixed 1T-MoSe2 and TiO2 nanotubes/MoSe2 for hydrogen evolution from light driven water splitting. The heterojuntion between silicon doped TiO2 nanotubes mixed 1T-MoSe2 phase exhibits pronounced activity in absorbing high light and speed up the electron-hole pair to the surface, which is believed to be shown higher photocatalytic activities than that of TiO2 nanotubes. The hydrogen evolution rate of 167.6, 135.5, 0.46, and 0.35 µmol g−1 h−1 were noticed for Si-doped TiO2 nanotubes/1T-MoSe2, TiO2 nanotubes/1T-MoSe2, Si-doped TiO2 nanotubes, and TiO2 nanotubes, respectively, which inferring the potency of Si-doped TiO2 nanotubes/1T-MoSe2 as photocatalysts. In a different study, Xu and colleagues have evaluated the TiO2 anatase phase with different facets namely Tsheets (95% of facets exposed) and Tcuboids (less {100} facets exposed) in order to make comparison for hydrogen evolution from water splitting. The Tsheets exhibits higher photocatalytic hydrogen evolution of 362 μmol·h−1 than those Tcuboids (79 μmol·h−1), which is almost 4.6 times higher than its Tcuboids. Facet reactivity and surface defects can influence on the photocatalysis. It is worth to note that with more {100} facets exposed on Tsheets, the more 5-coordinated Ti atoms along with oxygen vacancies can be offered on the surface to work as active site for water splitting in making hydrogen [149].

In photocatalysis research, the overall water splitting with the aid of light illumination is not yet fully understood because the complication and the unresolved scientific challenges of the processes put further questioning on sustainable and practical implication of that technology [17]. The underlying mechanistic relationship between the surface phases and crystal structure and photocatalytic activity becomes the one way in answering many of unsettled issues in PC-OWS [17, 156]. As we have seen throughout this review that the surface-phase largely affects the photocatalytic activity indeed because the phase junction is likely to improve the electron conductivity and supress the charge-carrier recombination rate what we will discuss in depth in the following sections.

In order to prevent the electrons-hole recombination during photocatalysis, it would be very fascinating to design and synthesize the photocatalytic materials with different phases ratio, that can maximize the synergistic effect of them as well enhanced the photoactivities of the phase junction. The photoactivity of the phase junction is also affected by the charge transfer processes between the different crystal phases. Therefore, constructing a well-matched and nondefective interfacial structure can not only highly desirable in experiencing effective interfacial charge transfer but a prolonged lifetime for electrons and holes could also realize in photocatalysis. The metal oxide Ga2O3 semiconductor have four ploymorphs: α-, β-, γ-, and ε-Ga2O3, which are highly attractable photocatalysts for overall water splitting reaction [157]. Upon calcination one can convert all other phases into β-Ga2O3 phase which is thermodynamically most stable one [158]. Literature snapshot indicates that the overall photocatalytic water splitting has been scrutinized deliberately on α-Ga2O3, β-Ga2O3 and mixed phase of them [159]. Jin and associates [160] have investigated the phase-mixed γ/β-Ga2O3 as photocatalysts in order to understand the effect of phase junction on overall water splitting reaction. They anticipated that the phase-mixed γ/β-Ga2O3 could drive the photocatalytic activity in a progressive manner due to the accelerated charge separation on the phase junction. Of the prepared samples, the γ-Ga2O3 phase along with Rh0.5Cr1.5O3 cocatlayst manifests a 67 μmol m-2h-1 and 30 μmol m-2h-1 of HER and OER activity, respectively. With the complete conversion of γ phase into β phase, a considerable photocatalyic activity was attained individually for HER (105.6 μmol m-2h-1) and OER (49.3 μmol m-2h-1) [160]. It was argued that with the enhancement of β phase into the samples, the photocatalytic activity was improved because the evolution of disordered structure during the phase transformation. The evolution of disordered structure is likely to be relevant with inherently defective spinel structure of γ-Ga2O3 phase rather than the lattice mismatch factor. The formed defects in phase-mixed γ/β-Ga2O3 might be helpful in recombining of an electron on a donor favoured by an oxygen vacancy while the hole on an acceptor favoured by either a gallium-oxygen vacancy pairs or gallium vacancy [160]. However, the contribution from the formed interfaces may reflect different results for overall water splitting reaction, taking interface between α-Ga2O3 and β-Ga2O3 as example. It was posited that the photocatalytic performance on the phase junction of α-Ga2O3 and β-Ga2O3 was higher than that of phase junction between γ-Ga2O3 to β-Ga2O3 since the disordered structure in γ-β phase junction of Ga2O3 works as defect sites and accelerate the charge carrier’s recombination processes, negating the expected efficiency for the overall water splitting reaction [159].

The formation of α–β phase junction and appearance of both phases on the surface are determined to be crucial in proliferating the mobile electrons which is therefore increasing the photocatalytic activity. Wang and colleagues [159] have examined the α–β phase junctions of Ga2O3 in water splitting reactions in presence of light and marked that the photoactivity was higher than stand-alone α or β phase structures. With the α–β phase junctions of Ga2O3, the figure of merits was reached up to 3 or 7-fold higher rather than those individual α-Ga2O3 or β-Ga2O3 phase. Even, the photocatalytic activity of the α–β phase junction samples was much greater than that of mechanically mixed α-Ga2O3 and β-Ga2O3 samples, which is almost equal to the summation of individual activities of α-Ga2O3 and β-Ga2O3 phases [159]. Looking at the microscopic analysis, it was demonstrated that neither the particle size nor surface area was believed to be the reasons in achieving high photocatalytic activities, but it was the presence of α–β phase junction. The formed junctions’ facilities the ultrafast electron transfer at approximately 3 picoseconds (ps), which is much speedy than the recombination (>1000 ps) and the trap processes (14-32 ps). Additionally, the lifetime of the photoinduced electrons in the microsecond timescale on the α–β phase junction is much higher than the individual α-Ga2O3 or β-Ga2O3 phase. It was good for these long-lived photoinduced electrons to participate in surface redox reactions, which is thus to increase the overall photocatalytic activity (Figure 15) [159].

Yet the highly active α-β phase junction can provide only qualitative information by means of spatial separation of photoinduced electron-hole pairs, leading to long-lived charge transfer state which is beneficial for OWS. The dynamic relationship between the phase junction and its photocatalytic activity is needed to grasp such that the fabrication and engineering in more effective semiconductor-based photocatalysts may reveal the underlying intrinsic activities. Number of unanswered questions, for example, what is the effect of lattice misfit and strain of the interfaces on energy band alignment, and how bonding networks near the interfaces could impact on the band mismatch within the charge depletion layer are far less well understood. Ju and co-workers [161] have studied the α-β phase junction theoretically to uncover these questions because strain-dependent energy band assignment and bonding network near the interfaces are crucial factor in tuning the photocatalytic activity of the junction. They used potential-line up approach in determining the band alignments of the α-β phase junction of Ga2O3 (Figure 16). It is evident that the electrostatic potential is localized in the region with 1 nm width that is in parallel with charge depletion regime, and the asymptotic macroscopic average of the β-phase is lower than that of α-phase (0.35 eV). The valence band offsets are much higher than the conduction band offsets (Figure 16). Even it’s too low, the conduction band offsets (0.07 eV) cannot be ignored since the lattice strain and mismatch of the two phases caused this primarily [159]. The effects of lattice mismatch are significant because atoms induce to rearrange near the interfaces and phenomena like defects appeared. With small driving forces, the conduction band offsets are unable to shift the electrons across the junction while the adiabatic mechanism for electron transfer at the interface coupling is suggested [161]. Analyses of the theory indicates that the band gap between the conduction band and valence band is large enough to afford the oxidation potential to get O2 from water oxidation and reduction potential to get hydrogen from proton reduction [162]. The relative energy levels position on both sides of the junction is subjected to the band offsets, which accounts the confinement potential for charge carriers across the junction, is one of the important parameters in tuning the photocatalysts. Basically, they are discontinuities between the CB minimum or VB maximum of each semiconductor at the common interface. To be fully extent for the band bending, the catalytic particles size should be less than or equal to twice the width of the space charge region, which can be the descriptor for bonding network near the interface on the band offsets.

Being ultrathin in thickness, the layered nanosheets is appearing as an emerging class of new materials having wealth of unusual physical characteristics which is advantageous in increasing the photocatalytic activity and long-term durability as well [163]. Zhang and colleagues [164] have synthesized free-standing single-layered nanosheets of γ-Ga2O3 phase using hydrothermal protocols in absence any kind of shape controlling agents. The surface defects and hydroxyl group passivation are thought to be the prime reasons for structural stability of single-layered γ-Ga2O3 nanosheets. Assessment was carried out over the prepared monolayers samples and found that a 312.5 and 67.5 μmol of hydrogen and oxygen were noticed over the course of 4 hours reaction at controlled pH [164]. The figure of merit of monolayer γ-Ga2O3 phase for PC-OWS was at least one-fold greater than that of bulk γ-Ga2O3 samples (25 μmol of H2). The rationale for this activity was related to ultrathin structure, which enables shortest diffusion lengths of photoinduced charge pairs and provide proliferate number of active sites due to large surface area [164]. In addition, the photocatalytic activity of the monolayer nanosheets was kept unchanged after three cycle runs. However, the formation rate of oxygen and hydrogen reduced over the course of reaction time while recovering the PC-OWS was done after evacuation. The reasons for the reduced formation rate was the reverse reaction of H2 and O2 into H2O with extended reaction time, making further barrier in formation of H2 and O2. Results indicate that apparent quantum yield of the γ-Ga2O3 monolayers is 0.35% at 250–264 nm. Nevertheless, the pH has significant effect on the surface charge of photocatalysts in inducing the electrostatic attraction or repulsion between the catalyst's surface and the reactant molecules and subsequently, increases or prohibits the photocatalytic reaction rate [165]. In acidic environment, (pH ≈3.2), the formation of both O2 and H2 decreased significantly while there is no change in the formation of the gases at pH ≈10.1. On further increasing the pH to 13.2, the gases can form rapidly which is comparable to that neutral solution. This is more likely at high pH values, the proliferate quantity of physisorbed OH− groups can participates in the photoinduced charge carrier’s separation process, which is thus facilitated the γ-Ga2O3 monolayers to get involved in O2 uptaking and hole scavenging in producing oxygen [164].

As we discussed previously that TiO2 have three phases: anatase, rutile, and brookite, where the brookite phase is unprecedented in generating H2 and O2 over others in a photocatalytic cell system. Complexity regarding the photoelectrical activity over some preferred phases than others remain elusive yet, and the scenario is more likely exacerbate for anatase and brookite phases when they are in photocatalytic system. Li and colleagues [166] have studied the PC-OWS and tested the phenomena of the three phase of TiO2 semiconductor from both thermodynamics and kinetics standpoints. Nor anatase or brookite was able to produce H2 and O2 at standard experimental conditions while contribution for PC-OWS may come from extended UV light illumination. Clearly, a significant PC-OWS was observed on rutile phase. The varied results over these phases are caused from the different crystalline phases. Answering the questions on anatase and brookite inactivities hinged on presence of the deep trapped states above the valence band level of TiO2, which can reduce the potential of photoinduced holes. The two-electron process is much preferable for photoinduced holes in forming OH• radicals from H2O molecules rather than four-electron process for O2 production directly. Upon UV light irradiation, these trapped states are slowly declined so as to enlarge the overpotential for water oxidation and consecutively produce O2. Looking at rutile phase, there is no trapped states above the valence band level and hence, it has to be enough potential for water oxidation and proton reduction [166].

Phase transition can change the band position from its original point, and this can be seen a band edge engineering approach alternatively. Scheelite monoclinic BiVO4 (m-BiVO4) is known as a well-documented photocatalysts having conduction band edge (CBE) is at more positive potential than the potential of water reduction, show incapability to generate H2. While it is apt at O2 evolution easily under visible light irradiation thanks to the proper valence band edge (VBE), its disadvantages, for example, weak surface adsorption properties and poor charge transport characteristics put it back to reconsider its photocatalytic activity further. Jo and group’s [40] have attempted to raise the CBE of yellow colored m-BiVO4 through a phase transition by utilizing both In and Mo dopants, getting a greenish colored Bi1-XInXV1-XMoXO4 compounds (GBVOX; x = atom ratio of In and Mo), which in turn, has ability to split water into O2 and H2 in presence of visible light in the absence any sacrificial reagents. DFT analyses reveal that In3+/Mo6+ dual doping induces the phase transformation into a mixed phase of monoclinic BiVO4 and tetragonal BiVO4 from pure monoclinic BiVO4 phase, which is responsible for growth of unit cell volume, increased compressive lattice strain, raised up the CBE, and widen the band gap as well. The authors explained that how this dual doping can influence the H2 and O2 evolution rate and pointed out that there is an optimum level of doping concentration for both metals which triggers the OER and HER simultaneously but the rate determining step is controlled by the water reduction process. Indeed, the best-performance photocatalysts, GBVO0.10, is a mixer of monoclinic (m) BiVO4 and tetragonal (t) BiVO4 phases, where approximately 60% is tetragonal BiVO4 phase. From surface energy perspective, the formation energies of In3+/Mo6+ dopants in *m*-BiVO4 and *t*-BiVO4 are 1.31 eV and 1.79 eV respectively, while the former one is independent of lattice strain and the later one is dependent on cell volume variation. The formation energy of In3+/Mo6+ dopants in *t*-BiVO4 is associated with cell volume of 1.407 Å while the cell volume for *m*-BiVO4 is 1.253 Å. When the cell volume decrease, the formation energy of In3+/Mo6+ dopants in *t*-BiVO4 decreases, even its get smaller than that of *m*-BiVO4 with cell volume less than 1.320 Å. Additionally, when the cell volume decreases below 1.254 Å, the total energy of doped *t*-BiVO4 decreases as well as compared with undoped *t*-BiVO4. This further verifies that the formation energy of In3+/Mo6+ dopants is accelerated within *t*-BiVO4 as compared with *m*-BiVO4, as the cell volume getting smaller to smaller. Finally, a stable *t*-BiVO4 phase can be realized with doping than without doping, which increases the performances of greenish colored Bi1-XInXV1-XMoXO4 compounds for PC-OWS.

Their excellent physical properties, for example, ion-exchange, intercalation, and catalysis, the Ruddlesden-Popper phases (RPP) with generic formula of (A2) ʹ [A*n*-1B*n*O3*n*+1] have gained considerable attention as photocatalysts for water splitting, where Aʹ is H or K, and A is La2/3 or Sr. These layered structural materials utilize their interlayer space as reaction sites, where the electron-hole recombination process could be nullified by the physical isolation of the photoinduced electron and hole pairs [167]. To confirm such hypothesis, Shimizu and colleagues [168] have prepared a series of RPP hydrous layered photocatalytic materials H2La2/3Ta2O7, K2La2/3Ta2O7, H2SrTa2O7, La2/3Ta2O3, and KTaO3 for H2 and O2 evolution from water splitting. Results indicates that hydrous catalytic materials show superior activity than anhydrous materials like La2/3Ta2O3, KTaO3, while characterization studies revealed that the high performance of the hydrous photocatalysts is due to the presence of their hydrated layered structure, which can work as a host for photogenerated electrons and holes. Introduction of Ni within the interlayer space increases the activity of H2La2/3Ta2O7 materials while there was no improvement observed for H2SrTa2O7 catalysts. Actually, the highly disperse Ni species act as active sites for H2 evolution during photocatalytic water splitting.

Layered perovskite photocatalysts have proven to be effective in producing hydrogen from water splitting. Li and co-workers [169] have highlighted a new series of layered perovskite photocatalysts, ABi2Ta2O9 ( A= Ca, Sr, Ba) while orthorhombic SrBi2Ta2O9 catalysts shows superior activities as compared with that of tetragonal BaBi2Ta2O9 catalysts. Computational studies reveal that the direct band gap feature of these catalysts have significant effects on the hydrogen production and the orthorhombic phase was ascribed to have a greater extent effective states available for the photo-induced electrons and holes. Additionally, Zou and colleagues [170] have reported a series of novel solid photocatalysts, BiTa1-xNbxO4 (0≤X≤1) with different phases like triclinic and orthorhombic. In a pure water splitting under light irradiation, they have found that the triclinic phase shows less activity than that of orthorhombic phase because the band gap of orthorhombic phase is much narrow than that of triclinic phase. The narrow band gap accelerates the exciton transfer from valence band to conduction band more easily. In terms of hydrogen production, it was shown that a 41µmol h-1 product was obtained with composition of x = 0.2, which are one of the studied orthorhombic phases.

Application of clean inexhaustible solar energy in hydrogen production from overall water splitting is deemed to be highly attractive means while consideration has been given to the development of low-cost and environmentally benign semiconductor materials [171]. To date, a variety photocatalysts have been employed in this process and remarkable advancement in this field has been reported. Yet a proper narrow band gap and their position is critical set demand in this process what can be tuned by fabricating and designing the different phase materials. Such preparative strategy will intensify the efficient photogenerated charge separation and the migration to the reactive sites. In the following section, however, we will emphasise a variety of phase materials for overall water splitting as well discuss the main underlying mechanism for them.

Merging both light harvester and charge carrier guider in a single system is known as photoelectrochemical (PEC) cell, which has shown promising technological effectiveness in utilizing solar energy. Development of PEC cell is being continuously investigated in order to increase the charge separation and transportation at the interface [172]. Happening of water oxidation or hydroxyl ions is necessary in PEC in order to provide enough source for protons and electrons to get in the desired reaction. Substantial research has been directed towards semiconductor based photoanode and/or photocathode materials in booming up the charge carrier separation and transportation, highly stable and catalytically active for HER and OER and thus enhancing the overall water splitting reaction efficiency. Photoelectrode (anode and/or cathode) materials, however, play central roles in overall water splitting reactions, which forms H2 and O2 as a product [173].

To verify the effect of different phases of MoS2 on the PEC performances, Pi and colleagues [174] have fabricated the three-dimensional (3D) photoanode with exfoliated MoS2 nanosheets on TiO2 nanorod arrays (TiO2 NAs) by using both hydrothermal and drop-casting methods. Among the prepared samples, the TiO2 NAs/1T-MoS2 composite show higher photoelectric conversion efficiency for an optimized mass loading of 1T-MoS2 phase than those of TiO2 NAs/2H-MoS2 and TiO2 NAs. A photocurrent density of 1.91 mA/cm2 was experienced with TiO2 NAs/1T-MoS2 composite, which is far inferior to those of TiO2NAs/2H-MoS2 counterpart (1.12 mA cm-2) and TiO2 NAs (0.42 mA cm-2). The plausible reasons for that improved catalytic performance was ascribed to the strong interaction between the 1T-MoS2 phase and TiO2 NAs and superior conductivity of 1T-MoS2 phase. The calculated electrical conductivity for 1T-MoS2 phase was about to be 3500 S/m, while 2H-MoS2 nanosheets exhibit an electrical conductivity of only 1.43 S/m. This is in line with the fact that the 1T-MoS2 is metallic, whereas 2H-MoS2 is semiconducting. Therefore, the photoinduced holes can move into the 1T-MoS2 nanosheets from TiO2 NAs demonstrating improved separation efficiency. In addition, the TiO2 NAs/1T-MoS2 composites have longer endurance than those other prepared samples. With TiO2 NAs/1T-MoS2 composite, a photocurrent of approximately 1.79 mA cm-2 (>92% of the starting current) was remarked over 12 h PEC test, while this percentage is only 87% for the TiO2 NAs and 82% for TiO2 NAs/2H-MoS2 [174].

A promising technique is appeared in tuning the band gap of metal oxide that is the hybridization of O 2p valence orbitals with a foreign element with high-lying valence orbitals, generating shallow valence bands in wide band gap metal oxides. Lou and colleagues [175] have studied this technique by inserting Bi3+ cations into anodized MoO3 thin films at control rate, which caused to form ternary γ Bi2MoO6 thin films along with shallow valence bands and reduced band gaps and used as photoanode for PEC water splitting devices. Two phases of ternary γ Bi2MoO6 thin films are associated with the bismuths precursor concentrations and hydrothermal temperature where low concentration provides γ(L)-phase Bi2MoO6 and a high-temperature-phase γ(H)-Bi2MoO6 for high precursor concentrations. Characterization studies show that as compared with MoO3 (*E*g = 3.4 eV), the band gap for both γ(L)-Bi2MoO6 and γ(H)-Bi2MoO6 is reduced to 2.7 eV and 3.05 eV, respectively [175]. This is more likely that the generation of higher-lying O 2p valence band maximum is the driving force in band gap reduction for γ(L)-Bi2MoO6, while the hybridization of the Bi 6s orbitals with the O 2p valence orbitals induce the lower valence band maximum potential for γ(H)-Bi2MoO6 thin film. In regarding photoactivity, the highest photocurrent density was observed with highest γ(L)-Bi2MoO6 concentration. Highlighted reasons for this activity were as follows: 1) the formed trilayer Bi2MoO6/MoO3 heterostructure allows smooth entrance of photoexcited charges from the surface generation sites into the charge collection sites at the Mo substrate, thus affording minimum charge carrier recombination rate, and 2) the MoO6 octahedra-coordinated γ(L)-Bi2MoO6 have large conduction band allowing rapid separation and migration of delocalized charges [175].

An individual search for PEC-OWS was done by Chemeleski and co-workers [176], who prepared amorphous FeOOH (a-FeOOH) catalysts for OER in PEC cell. With 10 nm thick films, a-FeOOH catalysts display an overpotential of 550 mV in reaching 10 mA cm-2 demonstrating a comparable photocatalytic activity. Because the thinner films, it absorbs less than 3% of the solar photons (AM 1.5 G) along with energy larger than 1.9 eV, and work as a protective layer separating the solution from the solar absorber. In a three-electrode set up, the a-FeOOH/amorphous-Si (a-Si) device attain a total water splitting efficiency of 4.3% at 0 V vs RHE and was kept its efficiency over the course of 4 h testing.

In PEC system, the charge transport processes between the conducting substrate and catalytic materials is important which implies to rationally fabricating the phase-junction for that analysed materials. This carries substantial significance because when photogenerated charge carrier try to transfer from catalytic materials to conducting substrate, a dramatic recombination’s rate of the photoinduced electrons and holes may realize [185]. In such a case, one can design the phase-junction to prolong the lifetime of the photogenerated hole and electrons and thereby, improving the photoactivity. We can consider two types of TiO2 phase junctions as PEC photoanode-(a) rutile nanorods over anatase films and (b) anatase films on rutile nanorods along with fluorine doped tin oxide (FTO) substrates for PEC-OWS [177]. As explained elsewhere that for the phase junction (a), the photocurrent density and onset potential were increased since the photoinduced electrons shifted to anatase films from the rutile nanorods, while a decline in the performance for water splitting over the phase junction (b) was marked as shown in Figure 17 [177] . In order to get unidirectional charge carrier migration and reduce the defects sites at the interface, it is thus needed to tune the phase alignment configuration which would increase the PEC-OWS performance. Taking three types of anatase and rutile phase alignment configurations as photoanodes in PEC-OWS system: random alignment of various phases (Type A), rationally ordered phase alignment (Type B), and ordered phase alignment in a reverse configuration (Type C) [178]. By checking the band position, it was rationale that the charge recombination rate was higher in type A and type C than that of type B, resulting in improved photocurrent density over type B as shown in Figure 17. Likewise, the phase junction between type B and TiO2-AR (calcined with oxygen gradually) exhibited higher performance in terms of charge separation and migration [178]. Apart from this finding, the interface between type B and TiO2-dAR (calcined with oxygen in two step) causes to slightly enhanced the charge carrier separation and migration to the reactive sites because the presence of interfacial dislocation. In such a situation, the CB holds energy barrier for excess minority carriers so that electrons can migrate to the reactive sites as shown in Figure 17 [178].

The beauty of the structural phase materials would heighten when one can constructing the phase junction by considering the periodic arrangement of various crystal phases along a preferred orientation. Because at atomic level the vectorial separation and transfer of the photoinduced charge carriers utilizing periodical phase interfaces could improve the photocatalytic performance for H2 formation. One of the examples in this case would be the twin-induced phase junction between the CdS and Cd1-xZnxS [179, 180]. An examination with Cd0.5Zn0.5S nanorod photocatalytic materials reveals that long-range ordered twinning planes with preferred [111] orientation can be efficient in separating photoinduced charges and contributed to prolonged lifetime of the photogenerated holes and electrons. Such twinning superlattices can be utilized to obtain alternating other dense homojunctions such as cubic zinc-blende (ZB) and hexagonal wurtzite (WZ) along that orientation. As is seen from Figure 18 that the boundaries of the twinning Cd0.5Zn0.5S nanocrystals suddenly abrupt the continuity of the ZB lattice structure while numbers of WZ segments distribution in the ZB lattice was noticed. Interestingly, it can be observed that a parallel homojunctions like ZB-WZ-ZB in a real nanocrystal may be realized with periodic arrangement and dense distribution as shown in Figure 18 (b). The up shift of both CB and VB energy levels for WZ segment were higher than that ZB segment, which separates the photogenerated holes and electrons spatially to the ZB segment, i.e, away from the twin plane and to twin plane on WZ segments. It is recognized that the in-built interface behaves as Type II staggered band alignment. Therefore, the large distribution and the close interconnection at the atomic level of the homojunctions of ZB and WZ is somewhat different than other heterogeneous junctions which can potent only separating either holes or electrons alone. However, the formation of such homojunctions is responsible for excellent photocatalytic activity in H2 production by accelerating the vectorial transfer of the photoinduced charge carriers [179].

The concept in generating valuable chemical fuels from CO2 reduction under photocatalysis has been adopted over the years which involves multiple electron transfer processes. One of key assessing parameters in photocatalysis for any given materials is the Faradaic efficiency, which dictates that an active catalyst may experience low overpotential to drive the reaction in the forward direction for the targeted yields. In CO2 cases, it is thus needed to design the photocatalytic materials that have as small of an overpotential as possible while one can observe a substantial volume of the products. While much efforts have been devoted in designing an active photocatalytic material, still there remain space to be workout. Having alternated electronic band structure, the phase materials is highly examined in CO2 reduction while we have reckoned many underlying issues remain to be unresolved. The following section will discuss any such challenges and provide some new insights in CO2 reduction into valuable chemical fuels.

We pretty much describe how HER works on electrochemical and photoelectrochemical approaches while we intend to rekindle the idea also here that how different phases and their engineering at atomic scale could amplify photocatalytic activity which, therefore, improve the end yields as well as stability. The CRR over potential semiconductor with appropriate band gap window has so long been sought. Yet the main mechanism for CRR remains less understood because of its thermodynamics inactivity and hence, multi-electrons (typically 2-12 electrons) reaction process involvement depending on the reaction environments [181].

As is seen in Figure 19 that there are numbers of reactions processes involved in PC-CRR. Unlike photodriven water splitting, the CRR proceeds by striking solar energy (photon energy) on the surface of semiconductor which should have energy (Ehʋ) equal to or higher than its bandgap (Eg) [182]. The bandgap excitation (photoexcitation) pumps the electrons in CB and holes in VB, which work as the active sites for photo-reduction and photo-oxidation, respectively. CB is the lowest energy band where no electron exists at the ground state and VB is the highest energy band which occupied by electrons. The electron-hole pair can move to the surface, happening combination at trap sites (recombination process) by means of radiation or non-radiation approaches [183]. Additionally, these electrons can move on the semiconductor surface where they can react with surface adsorbed species, CO2, but this can be realized when the recombination process is much slower during the transitions [184]. Since CO2 is thermodynamically very stable and inert so as to the reduction cannot be done by all surface reaching electrons. Apart from semiconductor contributions, the catalyst needs to be effective too, meaning that it should have electrons with higher energy than that of reduction potential of CO2. For an ideal photocatalytic system, the position of CB should be well above the reduction potential of interest at controlled pH, while the position of VB should be well below the oxidation potential of water oxidation. The first step in the photocatalytic CO2 reduction is the formation of electron-hole pairs, i.e. excitons, excited by incident photons. After band excitation, the pairs should be separated spatially with minimizing their recombination, and the separated electrons and holes will activate reduction and oxidation process, respectively, at the interface and. Yet with few nanoseconds lifetime, the pairs is enough to activate and complete the redox reactions while the time scale of their recombination is two or three times greater than other electron processes which is known as one of the major rate liming steps [185]. Unlike the ORR, which yields only H2O or H2O2 as a major product, there are several CRR products such as methane, methanol, carbon monoxide, formate, formaldehyde and higher hydrocarbons (C2 and others) and oxygenates. As is noticed from Figure 19 that the potentials for methane and methanol is much lower which makes the CO2 reduction process more favourable from thermodynamic standpoint. Nonetheless, the kinetic analysis suggests that these reactions are not easy to achieve because they need more electrons while the yields of carbon monoxide, formaldehyde and formic acid can be realized with less electrons. In addition, the reactions need 2-8 electrons and protons to get the yields of interest are stave off the process from being implication. Any photocatalytic process which suppresses the electron-hole pair recombination would significantly improve the CO2 reduction efficiency [183]. The PC-CRR, however, suffers from low conversion efficiency because of several reasons where the mismatching between the solar spectrum and adsorption ability of semiconductor and very fast charge carriers recombinations are few of them [183]. Great efforts have been pursued to improve the semiconductor band gap matching with solar spectrum by means of engineering the surface of the semiconductor, changing the phases, defects engineering, doping and so on.

An important aspect during the photocatalysis is the activity of photoinduced holes because they produced as much as electrons in the system. The gathering of holes on the photocatalysts surface could exaggerate the charge carrier’s recombination rate resulting in reduction of electron’s lifetime. The most destructive role, however, that the hole can play is to initiate the photocorrosion if they are unable to be utilized properly during the photocatalysis. The holes could be consumed by supplying third party electron donor like water, hydrogen, methane, and alcohols while the synthesis process of artificial electron donor needs to be considered very carefully because it may cause more CO2 emission [186]. Among the third-party electron donor, water seems like more competitive because of its copiousness and inexpensive. The oxidation potential of water, however, is higher than that of CO2 reduction which implying that an ideal photocatalysts should have ability to oxidize water and reduce CO2 simultaneously but there is a dearth of that kind of photocatalysts [187]. In presence of water, the photocatalytic reduction of CO2 needs to split the water to continuously supply the hydrogen for hydrogenation which is very demanding in manufacturing value added chemicals. Yet the application of water as electron donor remains problematic because of its competition with CO2 in terms of reduction process. The thermodynamics and kinetics scrutiny window says that the reduction potential of water to hydrogen is 0.0 volts at pH=0 which is definitely much positive than most of CO2 reduction to carbon dioxide, formic acid and formaldehyde while the former one only needs two electron process and later one undergo with 4-8 electrons process. This is indicative that the generation of hydrogen is much suitable than other products generation through CO2 reduction. This is more likely that the reduction of CO2 in water is limited by its low solubility which indirectly increase the probability for electrons to meet and react with protons for HER rather than for both electrons and protons to meet CO2 for CRR. Therefore, the reaction selectivity is important in the case for CRR where modifying the photocatalyst surface, altering the exposed facets, introducing new active sites and directional charge driving force, etc., are subjected to that reaction selectivity [181, 183, 188].

We, here, aim at the exploration of PC-CRR into value-added chemical compounds under light irradiation while emphasis will be given on different phases of photocatalysts and how these phases can be achieved from laboratory manuals and what impact of these phases on the end yields of CO2 reduction processes. There's always been a kind of implicit understanding that the phase tuning could change the local electronic configurations of the materials which ultimately show improved physical and chemical properties that is essential for particular reactions of interest. Readers should be aware that there are growing number of articles about PC-CRR over noble and effective photocatalysts systems [185, 189], which we do not summarized here so far because the scope and limitation of this review article. By the end of this section, we tabulated (Table 3) some phase-based photocatalytic materials for CO2 reduction.

Yu and associates [190] have investigated the exposed {001} to {101} facets in anatase phase of TiO2 samples in PC-CRR for methane production. By combining DFT calculations and experimental evidence, they confirmed that the photoactivity of the CO2 is highly dependent on the ratio of the exposed {001} to {101} facets. It is also reported that the concentration of HF in sample preparation has significant effects as such the formation of methane put forwards until the quantity of HF exceeds the value of 6 mL, which oppositely reduces the photocatalytic activity of the samples. The accepted reasons were the large number of exposed {001} facets in anatase, which drive an electron overflow influence on {101} facets owing to their lower percentage. Therefore, the electrons on the {001} facets and within the interior are barely shifted to {101} facets and because of the rich availability of {001} facets, they can easily recombine with holes on {001} facets. Similarly, He and associates [191] have analysed anatase TiO2 catalysts with different morphologies, for example, nanoparticle, nanotube, and nanosheet for PC-CRR in presence of water. The anatase nanosheets show superior photoactivity than those nanotube or nanoparticles. The plausible reason is that the anatase nanosheet have highly energetic exposed {001} facets, which could promote the oxidative dissolution of H2O with holes, resulting in numbers of electrons availability in reduction of CO2 on {101} facets. An excess number of Ti3+ species caused from surface fluorination on the low-energy {101} reductive facets accelerated the reduction of CO2 to CO2– and prolonged the lifetime of photoinduced electron-hole pairs, which is liable for improved photocatalysis [191].

TiO2, one of the most known and experimented star semiconductor materials in photodriven CO2 reduction system which naturally have three ploymorphs/phases (a) anatase, (b) brookite and (c) rutile. Of these phases, the brookite investigation is less prevalent for CRR in the published papers than those anatase, rutile or mixture of them. The electronic structure of these three polymorphs has significant effect on the electron-hole separation processes. Theoretical analyses reveal that among the three polymorphs of TiO2, the anatase is indirect band gap in nature, while rutile and brookite appears with direct band gap. As compared with rutile and brookite phase, anatase has the smaller average effective mass of photoinduced electrons and holes, which makes possible for anatase to transfer electrons and holes from bulk side to surface side very quickly, resulting in the reduced charge carrier recombination rate and thus, increased the photoactivity for anatase [192]. It was shown that for anatase, the lifetime of electrons and holes were nearly an order of magnitude higher than that rutile [193]. Having indirect bandgap, the anatase drives the highest photoactivity by means of preventing the charge carrier recombination, which strikingly increases the diffusion path length for electrons and holes. As a result, the rapid translocation of the photon-excited electrons and holes from the bulk to surface was realized, where the photochemical reaction takes place. It is worth to mention here that how far an excited charge carrier can penetrate into surface sites from bulk-also depends on the higher electron’s mobility and longer lifetime of themselves. In this case, anatase is much superior than rutile phase because the surface penetration for charge carrier over anatase is about 5 nm, while rutile adopts nearly 2.5 nm, which makes sense that anatase is much potential than rutile polymorphs [68].

Liu and co-workers [52] have studied the photodriven CO2 reduction in manufacturing value-added chemical compounds like CO and CH4 in presence of water vapour reducing agents over defect-free and defective TiO2 anatase, rutile and brookite nanocrystals. The hydrolysis and hydrothermal synthetic methods were employed to obtain the three phases TiO2 selectively while an *in-situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was used to distinguish the CO2 adsorption species and reaction intermediates on anatase, rutile and brookite phase surface. Results indicate that the defective TiO2 phases show remarkable photoactivity as compared to defect-free TiO2 phases. Much of that role is likely to be given over to the generation of oxygen vacancies and Ti3+ on the surface, which induce the CO2 activation both in the dark and under photoillumination by forming CO2- intermediates [52]. The surface engineered brookite phase is reported to provide the highest CO and CH4 products following by anatase and rutile phase. The formation of oxygen vacancies due to defective brookite phase causing the rapid reaction of CO2- with adsorbed H+ or surface OH- groups and provide an alternative reaction pathway involving an HCOOH intermediates [52]. Briefly, the reaction mechanism ratifies that the water dissociation (Reaction 17) and the formation of CO2– (Reaction 18) while reaction 19 tells HCO3– intermediates have been observed on both helium (He) treated anatase and brookite phases. CO forms from the reaction between CO2– and H+ (Reaction 20) or self-transformation (Reaction 21) or direct dissociation by healing the VO sites (Reaction 22). However, the CO2- intermediates did not show up on He treated brookite phase under photoillumination with water vapour reducing agents [52]. CH4 can be produced via multi-electron processes (Reaction 23 and 27) by converting CO, surface HCO3- and HCOOH as shown in below.

The presence of defects at surface or at bulk in a structural phase-based photocatalytic material have positive intuition on the overall photocatalytic performance due to its direct influence on the electronic structure. During photocatalysis, the defects sites work as a recombination centers for photoinduced charge carrier and accelerate the overall reaction. It was reported that the single crystal of anatase before and after calcination treatment possessed much lower recombination rates for charge carriers than those for rutile single crystal. As rutile single crystal have higher density of bulk defects, thus it has higher probability to recombine the photoinduced charge carrier and reduced lifetime of them as well [194]. However, the presence of both defects at a time could improve the surface reactions further as well as photocatalytic activity for both anatase and rutile polymorphs. It was shown that when surface defects trapped the photoinduced electrons-holes upon light illumination, then it can migrate them to the reactive sites where they can combine with the electron acceptors/donors. By doing this, surface defects can play role in maintaining charge carrier separation for longer time while the electron-holes trapped by the bulk defects sites recombine each other because the unavailable reaction sites [194]. As compared with CB and VB states, the defects are helping in increasing the electronic states within the band gap since the weaker bonding at defects sites can alleviate the splitting between the bonding and antibonding orbitals. During photocatalysis, the photoinduced charge carrier follow the mid-gap states to reach either CB or VB, which controls the charge carrier dynamics known as surface states or trap states, if only when they sourced from surface defects [195]. It is improbable for charge carriers those lie in the deeper trap states to contribute on the surface reactions while those are in shallower trap states can contribute in the surface reactions. Therefore, the structural phase materials have different depths of trap states which can further change the lifetime of the charge carriers. Not only surface defects can do the variations surface trap states for photoinduced charge-carriers, but surface terminations also play role in varying the trap states in structural phase materials. Varying the position of the hole-trapping states in the band gap, it is thus possible to tune the photocatalytic materials for improved performance.

Kar and co-workers [196] have experimented the PC-CRR into methane (CH4) over pure rutile phase and mixed phases of anatase and rutile square-shaped TiO2 nanotube arrays from electrochemical anodization in water-based electrolyte (FANT-aq) and ethylene glycol based electrolyte (FANT-eg) at 750 ºC flame annealing. The FANT-aq sample produces a 156 µmol gcatalyst. -1 h-1 of methane while FANT-eg produces about 9.5 µmol gcatalyst. -1 h-1 of methane under solar light environment. The yields from the samples LANT-aq and LANT-eg were found to be 92 µmol gcatalyst-1 h-1 and 2 µmol gcatalyst-1 h-1, respectively. However, the flame annealing partially converted anatase phase into rutile phase in ethylene glycol based TiO2 nanotubes, which resulted in improved photoreduction of CO2 into methane. A suitable band position is necessary to start the photocatalysis and in this case, the flame annealing in oxygen deficient conditions may induce oxygen vacancies and Ti3+ states, which create sub-energy levels below the conduction band (Figure 20). These sub-energy levels reduce the energy needed for the excitation of electrons. The effective band gap subsequently decreases due to defects and sub-energy levels [196].

The phase conversion from anatase to rutile to brookite is said to be proven challenging yet because the ill-understanding of the applied processes and technologies even there are growing number of synthetic protocols are available [197]. It makes more believable that coexistence of phases in TiO2 photocatalysts could open up the doors in achieving higher photoactivity rather than pure anatase or rutile phase since a synergistic phenomenon between them may need to realize. Benavides and colleagues [197] have achieved various phases (anatase and/or rutile) of TiO2 by varying the laser power density incident on a film of amorphous TiO2 nanoparticles which prepared by means of an incomplete nonhyrolytic sol-gel ester elimination reaction between titanium isopropoxide and oleic acid. The motivation was the low-power-assisted photoactivation of TiO2 films at room temperature. The microscopic studies reveal that a critical particle size (14 nm) of amorphous TiO2 nanoparticles can only allow the laser-induced phase conversion into anatase. With high propensity to absorb molecular oxygen, the TiO2 nanoparticles undergo successive phase transition from anatase to rutile. They insist that both phases may be patterned using the size of 25 × 25 mm2 of that system for a usable device. However, they claimed that without absence of any kind of dopant in the TiO2 film prior to photoactivation, the phase conversion is still achievable, and this work came out with such accomplishment that its easy integration with TiO2 can be suitable for many photoelectrocatalytic applications [197].

The anatase and rutile heterojunctions for photocatalytic processes have shown remarkable efficiency because of an improvement in charge carrier lifetime but such performance over anatase and rutile heterojunction is now questionable and necessitates to explore the more fundamentals in this area. It is important to look at what actually happens within these heterojunctions, especially what are the direction and efficiency of photoinduced hole and its impact on the photocatalytic function. Recently, Kafizas and associates [198] have studied the hole transfer processes over the anatase and rutile heterojunction in films by using transient absorption spectroscopy (TAS) protocols as a function of phase composition. The phase conversion from anatase to rutile observed above 600 °C but this conversion process is slow in nature. They have insisted that the photoinduced holes can be moved to anatase from rutile on submicrosecond time scales. Among the analysed samples, anatase and rutile composite shows an almost 5 times increase in anatase hole yield due to such hole transfer mechanisms from rutile. The charge recombination picture at heterojunction surface is interesting showing an intermediate decay dynamics (*t*1/2 ≈ 4 ms) between that of pure anatase (*t*1/2 ≈ 0.5 ms) and rutile (*t*1/2 ≈ 20 ms), which nullify the speculation that the synergistic enhancement in photocatalytic reactivity is caused by an enhancement in charge carrier lifetime solely [198].

Apart from TiO2 based semiconductive materials, the NaNbO3 appears to show promising photocatalytic performance. With typical perovskite structure, NaNbO3 displays primarily two types phases (a) cubic (c-NaNbO3) and (b) orthorhombic (o-NaNbO3). Li and colleagues [143] have examined the photocatalytic performance of c-NaNbO3 and o-NaNbO3 phases and reported that the CO2 reduction activities over c-NaNbO3 phase outperformed the o-NaNbO3 phase under UV-vis light illumination [199]. Theoretical analyses unravel that the electron-hole pair generation and separation is highly accelerated due to the unique electronic structure of c-NaNbO3 phase. They stated that the highly symmetry in the crystal structure could improve the photoinduced excitation and transfer as well (Figure 21).

In another study, Li and colleagues [200] have testified c-NaNbO3/o-NaNbO3 phases for PC-CRR and found that a 30% and 200% enhancement in photoactivity over the mixed phases junction than those stand-alone c-NaNbO3 phase and o-NaNbO3 phase, respectively. In brief, the photo activity is higher on c-NaNbO3 phase than o-NaNbO3 phase while the mixed phase junction synthesised between 450 and 525 °C exhibit much better activity than those c-NaNbO3 phase and o-NaNbO3 phase. The reason behind that is the phase junction could heighten the photocatalytic performances of NaNbO3. The phase junctions between c-NaNbO3 phase and o-NaNbO3 phase can promote the photoinduced electrons from the conduction band of o-NaNbO3 phase to the trapping sites on the c-NaNbO3 phase, dispelling the charge recombination rate on o-NaNbO3 phase and therefore, further increase the prolonged life time of electron-hole pair in the mixed-phase NaNbO3 junction. It is obvious that the charge transfer in c-NaNbO3 phase is much easier than o-NaNbO3 phase, which is proven to show higher photocatalytic activity than its counterparts. We hypothesise that the electronic structure of c-NaNbO3 has changed the charge carrier behaviours because the CB of c-NaNbO3 is more dispersive than those of o-NaNbO3 [143], indicating the smaller effective mass of the photoinduced electrons in c-NaNbO3. As a result, the electrons easily apart from holes and transfer to the reactive sites and thus, increased the photoactivity. In a nutshell, the mixed phase junction seems to play a vital role in increasing the propensity of charge pair’s separation and this is likely to improve the photocatalytic efficiency [200].

The redox reactions such as EC-HER, EC-ORR, EC-OER, EC-OWS, PC-HER, PC-OWS, PEC-OWS, PC-CRR, PC-AOPs, EC-AOPs, PEC-AOPs and FAOPs have significant scientific merits in clean energy conversion processes, for example, electrocatalysis, photoelectrocatalysis, and photocatalysis, in producing a broad range of chemicals and fuels and in environmental application for organic dye decomposition. Much effort has already been done and many more are being continued in order to develop an improved catalytic material in achieving high performances from respective processes. Focusing on highly active catalytic materials, the SPE-an engineering approach to tuning the innate properties and functionalities at nano-regime, depending on their various species and highly anisotropic structures; seems look like to increase the number of active sites and thereby, increasing the catalytic intrinsic activity which thus, essential for the said redox reactions system. The SPE strategies can be potential in tuning the atomic level thickness, reduced lateral sizes, direct band gap, generating sulphur vacancies/defects, crystal phase engineering and so forth. There are vast number of materials show phase(s) where the catalytic activity is significantly differing from one to another. Of the known phase-based materials, the MoS2 has been studied extensively in all format of redox reactions like above owing to its excellent thermodynamics’ understandings with hydrogen adsorption energy. Knowing the benefits of MoS2 with other similar materials, most of the studied redox reactions mechanism referred to electrochemical applications, while the less understood for photocatalytic applications. Having said that the limitations relating to HER, OER, ORR, are the sluggish kinetics and overall energy lose phenomena and thereby, influencing the overall efficiency of that process. Using renewable energy as an input, the CO2 reduction in presence of light not only produces value-added products but reducing the dependency on fossil fuels- a major hike in achieving effective energy technologies. This is a multielectron reduction reactions system need a number of various surface-bound reaction intermediates which just enlarge the process complexity from being practical applications. Given the tremendous achievement for the said redox reactions, there remain plenty room to work where SPE can envisage a major breakthrough in this fields yet. Further studies are also sought to demonstrate the in-depth details about the electrode-electrolyte interface that remain less understood to date. Studies like synthetic methods are also important in SPE framework while understanding the kinetics and reaction barriers of key elementary reactions over different phases is the frontier of current energy conversion processes.

Throughout this work, we have seen that MoS2 with 1T and 1Tʹ phases is laterally referenceable in electrocatalysis, photocatalysis and photoelectrocatalysis processes for energy and environmental application because of their structural properties. With differing electronic band structure and DOS, their application extends from water splitting to environment pollutants degradation while varied investigated results were reported for improved catalytic activities. In attaining high performances from electrocatalytic HER, many studies have oriented with the preparation of 1T MoS2 phase from its 2H phase and compare their activities with similar works, even with its bulk form. However, depending on the nature of the analysed reaction, the functionalized 2H phase can be more effective and show superior activity than 1T phase of MoS2, for example, in pollutants degradation. Apart from such experimental investigation, one may combine preferred phase(s) with preferred nanostructuring, which led to improve HER performances. For example, the intercalation of lithium ions into the van der Waals gap of MoS2, can transform the phase from semiconducting 2H to metallic 1T phase and may construct vertically aligned MoS2 nanostructure (nanosheets, nanorods, nanowall and so on) in increasing the catalytic performances. Another architecture would be in this line is forming the 1T/1Tʹ phase or 1T/2H phase with appropriate electrocatalysts, which can be tuned with surface functionalization resulting in unique physical and chemical properties that evolve from the quantum confinement and the surface defects. With SPE strategies, it is significantly important to increase the active sites in basal plane of 1T phase as compared with 2H phase since basal plane have more exposed surface areas, while increasing edge active sites is equally deserved. Making sulfur vacancy with strain engineering can be potential in booming HER performances. As a co-catalysts 1T phase with semiconductor materials is another approach that can spark the electrochemical activity of HER system. One of the promising strategies in boosting the HER activity is the construction of multimettallic nanomaterials with different phases, for example, the 4H/fcc-Au@MoX2 (X= Se and S). We find that such preparative strategy is unique and applicable for HER in acidic medium. Apart from HER, very few reported the ORR and OER with SPE strategies, demanding much more experimental works with variety of phase–based materials. Electrocatalytic OWS reaction has experienced with just 1T phase with hybrid nanostructure while the design of multiple heterointerfaces can unleash the intrinsic activities of electrocatalysts, and hence improve the OWS efficiency.

In photocatalysis, the obvious problems, for example, charge carrier recombination, light-adsorption range, quantum efficiency and so on, needs to be resolved yet since these issues are more likely related with photocatalytic nanostructural properties. Adding co-catalytic materials on semiconductor surface could improve the photocatalytic activities, providing more hydrogen reduction sites, and reduce the activation energy that ultimately accelerate the proton reduction. Designing the intraplane heterojunction with 2D semiconductor can provide facility in reducing charge recombination process because the different phases may enable diverse physical and chemical properties in the same plane, accelerating the HER performances. Also, such fabrication through van der Waals interaction minimize the Schottky barrier or even wipe out the schottky barrier, which is important for charge transfer on the surface. Phase-based perovskite catalytic materials may reveal potential for hydrogen generation under light irradiation.

The PC-OWS study has limited with mixed phase γ/β-Ga2O3 system yet leaving a significant room for improvement with other phase-based materials like 1T-MoS2 or similar, of course, a combination with versatile semiconductor could drive the photocatalytic activity in a progressive manner due to the accelerated charge separation on the phase junction. The construction of the phase junction with periodic arrangement of various crystal phases along a preferred orientation is uniquely efficient in separating photoinduced charges and contributed to prolonged lifetime of the photogenerated holes and electrons. Because at atomic level the vectorial separation and transfer of the photoinduced charge carriers utilizing periodical phase interfaces what leads to improve performance for H2 formation from PEC-OWS. However, the scarcity of PEC-OWS studies with SPE opens a new route for the scientific community to work more in this fields. The CRR with potential semiconductor with appropriate band gap window is a requirement in photocatalytic system, while phase transition can change the band position from its original point and this can be seen a band edge engineering approach alternatively, which thereby essential in improving CRR efficiency. Proper utilization of the produced hole within the point of source is needed since it may increase the charge carrier’s recombination rate resulting in reduction of electrons lifetime. The SPE TiO2 sample is laterally applicable in photodriven CRR because of its typical three phases namely anatase, brookite and rutile, while the scenario for photoelectrical activity is more complex over some preferred phases than others that warrant further studies. The feasibility of other phase-based materials, for example, cubic and orthorhombic NaNbO3 have seen in order to increase the prolonged lifetime of electron-hole pair in the mixed-phase junction and hence, improve the CRR performances. With α-, β-, γ-, δ-, η-, and ε phases, MnO2 catalysts is frequently used in photocatalytic dye degradation due to the diverse d band gap energies and good adsorption ability towards the reactants. While brookite TiO2 shows less performance in PC-CRR, the higher photo degradation activity in PEC-AOPs, not just justify its structural properties efficacy but also the applicability for other photocatalytic processes. However, the 2D TMDs materials with different phases with semiconductor materials can also be a viable option in this regard and such advancement will further guide the scientific community with more understandings including both theory and experiment which will allow one to use the catalysts with near ideal efficiency and selectivity.

A knowledge of the SPE is of great significance to those studying nanomaterials for environment treatment. As reviewed, the surface properties, thermostability, conductivity, composition of the single or mixed phases have notable outcomes on the final properties and catalytic performance of the catalysts. Accordingly, it may be deliberative and desirable to improve or inhibit the phase transformation to select the more suitable phase or mixed phase mixture for specific application. The consideration of the mechanisms by which the phase transition is promoted or restricted will, in turn, enable us with the rational design of regulating strategies (e.g. annealing temperature, foreign ion doping) and help us predict the effects that these strategies are likely to have on the final materials. This eventually can facilitate the optimisation of the catalysts for efficient environment treatment.

To realize the fossil-free route to produce fuels and chemicals utilizing the above redox reactions require to design and architect the high-performance catalytic materials with improved activity, selectivity and durability while SPE could uncover broader physical properties of the catalytic materials such as the charge carrier separation and transportation in bulk and surfaces. For a given reaction system, the activity and selectivity of the catalytic materials can be achieved either by improving the structural properties to expose more active sites per unit or enhancing the intrinsic activity of each active sites. These strategies in improving catalytic activity and selectivity cannot be achieved straightforwardly rather they needs to be accounted simultaneously. Nano-to-atomic structural phase engineering allows to manoeuvring the nanostructure with a substantial fraction of exposed active edge sites, especially in MoS2 cases, which is a prerequisite for higher activity and unusual selectivity in a redox system. Opposite to this result, it was also observed that the basal plane of MoS2 could be catalytically more active than the 1T-MoS2 active edges sites. However, the nature of the reaction medium plays vital role in electrocatalysis, so does the strategies in improving catalysts activity and selectivity needs careful selection from many existing methods. Nevertheless, the extensive crystal phase engineering of MoS2-based catalysts over the years has been achieved remarkable advancement in improving materials activity and selectivity leave a plenty room for further progress yet. This will include the design of materials with higher fraction of active edge sites while reduce the kinetic energy barrier for the redox system which is a set condition to be known as active catalysts.

In parallel to electrocatalytic processes, the catalytic activity and selectivity in photocatalysis is largely dependent on light harvesting, materials suitable band gap, charge carrier separation and migration among many. We have seen throughout this work that SPE approach searched for tunable light harvesting phenomena which relates with the materials band gap engineering. In photocatalysis, the phase-dependent surface reaction mechanism is governed by the redox potentials of illuminated charge carriers what depends on electronic structure and the adsorption and activation ability of the surface atomic rearrangement towards reactant molecules. Such phase dependent reaction has one notable shortcoming and that is the recombination of the charge carrier before reaching the reaction sites. Therefore, with increasing the charge transfer and subsequently, reduce the charge recombination could be a promising pathway to tuning the photocatalytic performance. The electronic structures of photocatalytic materials in different crystal phases significantly affect the charge transfer behaviors so as to their selectivity’s towards final product formation. As we have seen for NaNbO3 within this study that the photocatalytic H2 evolution activity and selectivity over cubic NaNbO3 phase were almost twice those of orthorhombic NaNbO3 phase. Theoretical study of electronic structures reveals that the CB of orthorhombic NaNbO3 phase was less dispersive than that of cubic NaNbO3 phase, signalling a smaller effective mass of illuminated electrons in cubic NaNbO3 phase, which was responsible in increasing the photoactivity and the selectivity of the materials. Increasing the electron-hole separation time is an alternative means to pump up the photocatalytic activity of the materials. Taking Ga2O3 as an example, the enhanced water splitting performance was realized by engineering the α–β phase junctions on surface while the position of CB and VB of β-Ga2O3 were more positive than that of α-Ga2O3. Upon light irradiation, the photoinduced electrons migrates from α phase to β phase, while the generated holes tend to move from β phase to α phase due to the potential difference. Here, we noticed that photo-induced electrons and holes can be spatially separated and migrates in two different phases where they accumulated eventually. Adopting this strategy, one can reduce the charge recombination while improving the photocatalytic activity and selectivity in HER and OER. However, there are misleading information in the published articles-identifying a simple mixture of different crystal phase of the materials as phase-junction. As a phase-junction material, a well –defined interface between the different phases is required, which pulling up the electron-hole separation and hence, facilitates the photocatalytic activity for given redox reaction.

How long a catalytic material can be active and selective towards the products within the reaction system, is mainly dependent on the intrinsic activity of that materials which is directly a function of the electronic structure as well as density of the active sites. We recall them as stability here - one of the crucial indicators in determining the catalytic materials performance. In electrocatalysis, stability of the catalytic materials is a long-sought mystery and much efforts needs to be done yet. The reason is that the reaction medium in electrocatalysis either be in alkaline or acidic environment, resulting in subsequent dissolution and corrosion of the catalytic materials over the course of the reaction. In order to prolong the catalytic materials lifetime, the phase-transformation engineering is seen an option to reduce the sluggish reaction kinetics and enhance the active sites. A study, for example, shows that the selectively controlled synthesis of 1T-2H MoS2 phase junction has much more electrical conductivity than that of other phases which is beneficial to obtain enhanced HER electrocatalyic activity for about 500 days long run from water splitting. However, a deeper understanding and application of advanced computational studies and utilization of sophisticated characterization tools regarding the working states of the catalytic materials and the nature of their active sites is required in achieving progress in the field of electrocatalysis, especially in the context of stability.

Generally speaking, the stability of photocatalysis and photoelectrocatalysis is somewhat linked with the catalytic materials ability in absorbing light, charge transfer and migration as well as surface reaction through photocatalysts phase engineering. As long as the photoinduced charge carrier keep separated from being recombination and migrate into the surface where they can bind with the reactant molecule thereby forming products, the photocatalyst may recognize as long durable materials. To achieve such working functions for a given photocatalytic materials, the SPE could be effective in accelerating the charge kinetics because the electronic structure of the materials can affect the charge behaviours significantly. For example, the construction of 1Tʹ-2H phase junction of MoS2 is significantly boost the charge carrier mobility which increase the photocatalytic and photoelectrocatalytic performance as well the stability in water splitting reaction.

Overall, the development of phase-dependent catalytic materials has achieved much progress up to date, but there remain serious challenges to be researched in future. In hetero-phase engineering, the phase mixture ratio is still not precisely and designed controlled while in single-phase engineering, the biggest concern is the stability and purity of the desired phase. The activity of catalysts utilized in environmental treatment is highly influenced by their surface phase structure and chemical properties. In the future, the improvement opportunity is to induce and elucidate innovative methods for phase engineering. In brief, the study of phase engineering at the nanoscale would be focused on the following aspects in future: (1) developing refined technologies for phase transformations, to precisely regulate the band structure and the matching degree of the energy band of the heterojunction; (2) design suitable preparation methods to construct the multi-, hetero- or single-phase structure which could expose the desired crystal face at the greatest extent. Only in this case, the ROS activation occurred at the catalyst's surface could be studied qualitatively and reliably.

Generally, the redox reactions proceed within a system where solid catalytic materials remain contact with liquid and gas phases. A rich variety of elementary reaction and energy transfer processes befall at the solid-liquid-gas interface and such reactions is much more complex having relationship between each other. Interfacial surface reactions are critical for the redox reactions including water, hydrogen, and oxygen, in the sense that without knowing any detailed understanding about the relevant interfacial surface reactions, it is possibly strenuous work to design and modulate the proper catalytic materials. At interfacial junction (Junction –where three phases are met) many of the reactive intermediates formed and ready to be settled down as adsorbed species over the course of the reaction. Knowledge of the kinetics and dynamics of the formed reactive intermediates is the key to fabricating materials with enhanced activity. However, the reaction mechanism and their subsequent understanding in explaining the catalytic materials remain elusive yet, for example, the HER evolution mechanism and dynamics over 1T-MoS2 electrocatalyst mingled with different opinions and agreements. The reason for such variations is that the MoS2 is a polymorph material and its different phases show different electronic properties and mechanism so does examine the redox processes. Within this work, we have been highlighted that the 1T-MoS2 nanosheet possess improved electrical transport and higher charge transfer kinetics at the interface as well as high reactivity toward surface covalent functionalization. With DFT calculation, it was verified that the chemical treatment of the bulk MoS2 dispatches the higher tendency to bind H over the basal plane of 1T-MoS2 as opposed to 2H-MoS2. Another aspect of 1T-MoS2 nanosheet is to provide much more surface area with respect to edge portion which is beneficial to functionalize with the adsorbed H atom. In electrocatalysis with acidic environment, the adsorbed H atom play key role for overall redox reaction. The overall redox reaction rate is largely determined by the atomic hydrogen adsorption free energy on catalyst surface so-called ∆GH. Depending on the ∆GH values, the adsorption and desorption processes on the surface may limit the overall reaction rate. Ideally, an active catalyst for HER have ∆GH values close to zero, signalling that an active catalytic material binds reaction intermediate(s) neither too week nor too strongly. Reducing protons into hydrogen from HER in acidic environment may follow either Volmer−Heyrovsky or the Volmer−Tafel mechanism. Conversion of protons from the acid solution into adsorbed H (H+ + e- →Had) is referred as Volmer reaction which occurred very quickly. When a solvated proton from the water layer combine with one Had and form H2 (Had + H+ + e- →H2) which is known as the Volmer−Heyrovsky step while the reaction between two surfaces Had leading to H2, is known as Volmer−Tafel mechanism. It is worth to point here that Volmer−Tafel mechanism is largely related with the surface hydrogen coverage because there is no charge transfer involved with this process. Theoretical studies show that the HER mechanism is followed by the Heyrovsky reaction because the adsorption hydrogen energy for Heyrovsky step is much lower than for the Tafel reaction. This is indicative that the Heyrovsky reaction is proceed very rapidly over the 1T-MoS2 at an electrode potential of -0.22 V along with 25% hydrogen coverage. As opposed to Heyrovsky reaction, the Tafel slope is recognized as an intrinsic property of the electrocatalysts-largely determined by the rate limiting step and give hints for possible reaction mechanism of the HER. Based on same scale of ∆GH, however, some research group reported that both edges sites and basal plane of the 1T-MoS2 are effective for HER. Therefore, in future research, one should take care when considering the HER mechanism over phase-dependent catalytic materials and explain them in terms of the reaction products.

The surface reaction dynamics in photocatalysis and photoelctrocatalysis is complicated due to the involvement of light, band position of the analysed materials, redox properties of the photoinduced electrons and holes, excitons and so many. The complexity of the surface dynamics for the above processes is further extended when one can consider the crystal phase-dependent photocatalytic materials because different phases have altered surface atomic configuration. In photocatalysis, the catalytic reactions take place at first side while the charge carrier separation and migration are typically proceeded afterwards. The reactant molecules can adsorb on catalyst surface either by molecularly or dissociatively during surface reactions, followed by the addition of photoinduced electrons or holes to experience the half reduction or half oxidation reaction. After that, the formed products from the surface would desorb and diffuse to the atmosphere. In exceptional cases, the formed reactive intermediate(s) can back to the reaction site again and contribute the catalytic reaction further. As we said earlier that the surface atomic arrangement is the key factor in crystal phase-dependent reaction dynamics because such atomic arrangement could control the adsorption, activation of the reactant molecules as well as the reaction coordinates. Thermodynamically, for instance, the rutile (110) and anatase (101) facet is the most stable surfaces among many TiO2 single crystals, although other facets with higher surface energy can be realized with control thermodynamics and kinetics. It is set out that kinetically, the rutile (110) facet is more active than that of anatase (101) facet for water splitting. The surface energy possess by the rutile (110) for O-H bond breaking was nearly ~0.2 eV lower than anatase (101) facet. The validated explanation for this is the much favourable local bonding geometry of the surface. The surface structure of TiO2 have significant effect on the reaction pathway because the rutile and anatase have different geometry for oxygen. As compared with rutile, the anatase shows low photocatalytic performance in terms of oxygen evolution, justifying the O2 evolution on anatase surface followed by two electron migration pathways, which is less favourable and very much different from the single-transfer-pathway. The surface reaction in photocatalysis may be accelerated by means of defective photocatalysts because defective catalytic materials is subjected to the dangling bonds and coordinate with unsaturated atoms at steps, terraces, adatoms, vacancies and kinks, those are thermodynamically instable but provide stimuli to the reactant molecules adsorption and activation with the aid of photogenerated electrons or holes. It was reported that the formation of Ti3+ and surface oxygen vacancies on the surface can activate the CO2 reactant molecule by forming the CO2• intermediates, which remarkably increased the photoreduction of CO2 with water over defective TiO2. The defective brookite polymorphs shows excellent photoactivity in terms of CH4 and CO production which linked with their relatively lower formation energy of the oxygen vacancies and the presence of HCOOH intermediates. As we have pointed out that the surface reaction is largely dependent on the contribution from reactants source, radicals/intermediates, reaction pathway, diffusional dynamics of the formed products and transformation, while the redox properties of the light induced electrons and holes are also helping in activating the surface molecule. If the position of the CB and VB of the given photocatalysts are more negative or positive than the redox potential of reduction or oxidation, only then photogenerated electrons or holes can drive the surface reactions. In future, to understand solid/liquid/gas interface dynamics together with the reductive/oxidative properties of the active electrons/holes in the whole redox system would be a challenging but useful research strategy.

All the reviewed results have proved that structural phase engineering offers opportunities for doing both fundamental and technologically environmental treatment research. However, how phase engineering affects the activity of the catalysts for pollutants degradation is still complicated. Specifically, the dynamics towards the ROS activation occurring at the solid/liquid interface of various phases is unclear*.* From the perspective of the experimental characterization, the detailed phase transformation is also undera hazy situation. In future research, it is necessary to use the powerful in situ and transient technologies (e.g. in situ variable temperature EPR) to interpret the mechanism of the actual phase transformation and their ROS activationprocess. Besides, some specific phase structures (e.g., α-MnO2) can show robust efficiency for pollutant degradation under PC-AOP and FAOP, the essential distinction and relation of ROS activation with the same phase under different AOP configuration should be investigated. However, there are so many driving factors that need to be accounted during of photocatalysis because the photocatalytic materials synthesize utilizing various techniques and parameters, and different reactant may behave differently in the process of adsorption and activation on the photocatalysts surface.