Chapter 7

Conclusions and Future Scopes

7.1 Conclusions

In conclusion, we have successfully demonstrated the synthesis of various functional two-dimensional (2D) nanoarchitectures, which consist of synergistic hierarchical nanostructures with diversified functionalities for their applications in electrocatalysis and photocatalysis. We have favourably demonstrated that such novel nanoarchitectures can be developed using a one-pot hydrothermal method, which yields homogeneous, ultra-high pure materials with superior properties. On the other hand, SO_3H functionalizations of 2D-MoS_2 were delineated using a simple variation of precursor concentration ratio in a one-pot hydrothermal process. It needs to mention here that all the nanocomposites, nanohybrids, and the SO_3H-MoS_2 nanosheet are reported first time ever in this work. Incidentally, we observed that engineering of such nanostructures are immensely required to fine-tune the physicochemical properties with structure-function correlations for applications in different high-performance electrocatalysis and photocatalysis. In specific, designing such multi-component systems with enhanced electronic and catalytic properties involve diversified challenges in controlled synthesis and processing, modulating interface engineering, tuning surface chemistry, understanding reactions & growth mechanisms, etc. All these nanoscale archetypes were characterized to determine the morphology and structure, dimensionality, and degree of functionalizations, and finally used for electrocatalysis and photocatalysis. A chapter-wise summary of individual observations and conclusions are given as follows.

In chapter 3, the reduced graphene oxide (rGO) layer supported $MoNi_4/MoO_2$ nanorods were synthesized by using one-pot hydrothermal process followed by annealing at 500ºC. The nanocomposite exhibits the presence of both the $MoNi_4/MoO_2$ and rGO structures intact as designated via XRD, Raman and TEM/SAED data. The as-synthesized $MoNi_4/MoO_2$:rGO nanocomposites shows the active catalytic performance for hydrogen evaluation reaction (HER), as well as stable durability for more than 12 h in 1M KOH solution. The electrocatalytic HER performance of nanocomposite supersedes the efficacy of both the $MoNi_4/MoO_2$ and rGO, while graphene support provides a high surface area, conducting pathways for the electron transfer. Also, the edge-plane-like structure of catalytically active sites and localized surface defects of rGO contributes towards improving the performance of the overall HER efficiency of the nanocomposite, thereby, accelerating the charge transfer kinetics as well as lowering the diffusion coefficient. In general, this work fundamentally highlights the advancement on developing noble-metal-free electrocatalytic materials for hydrogen evaluation reaction (HER).

Chapter-4 demonstrates the development of a synergistic hierarchical structure consisting of $MoNi_4/MoO_2$ nanorods coated with vertically aligned 2D MoS_2 flakes for hydrogen evolution reaction. We used a hydrothermal method for synthesis where we obtained that $MoNi_4/MoO_2$ nanorod assembled with 2D flaky MoS_2 simultaneously improved the interfacial charge transport properties of the hybrid MoS_2:$MoNi_4/MoO_2$ structures, thus, acting as an active catalyst for enhanced HER. The as-grown 2D MoS_2 is a vertically aligned forest-like structure grown via a self-limiting hydrothermal process. The MoS_2 flakes are developed like flower petals-shaped structures with a size of ~300-500 nm and thickness of ~2-5 nm. Numerous structural characterizations, such as XRD, FESEM, TEM/HRTEM, and XPS, show that the synergistic nanohybrid structure forms with high surface area and distinct electrocatalytically active phases. As a growth mechanism of the formation of the nanohybrid structure, we found that initially, sulfur super-saturation occurred in the aqueous solution under elevated temperature and pressure, followed by the catalytic growth of 2D flaky MoS_2. We also obtained the formation of various active surface species, which we believe play a key role in enhancing the catalytic activities of vertically aligned MoS_2 on the surface of the nanorods. The electrochemical results demonstrate the extraordinary improvements in the performance of HER reaction of the nanohybrids compared to the pristine MoS_2 by lowering the overpotential, increasing the surface area, and enhancing the interfacial charge transfer kinetics. We further believe that this work will open a new research field and be applicable to other energy-harvesting and storage devices, including solar cells, batteries, fuel cells, supercapacitors, and many more.

Chapter 5 delineates with the development of in-situ -SO_3H functionalized MoS_2 catalysts with interlayer expanded features synthesized via a one-pot hydrothermal process with increasing thiourea content. Characterization techniques (such as Raman, FTIR, XPS, XRD, and TEM/HRTEM) endorsed the successful functionalization of MoS_2 nanosheets, where surface functionalizations and intercalations of -SO_3H functional group co-occurred with expanded interlayer distance via successive increase of thiourea. The 2D MoS_2 nanosheets produced using molar ratio 1:8 of $(NH_4)_6Mo_7O_{24}$. $4H_2O$:CH_4N_2S showed the 4.84% of -SO_3H functional group contained in MoS_2 nanosheets, which demonstrated the high-performance electrocatalytic activity for HER. We also found that further increase in the thiourea ratio decreases the % of -SO_3H functional group and transforming -SO_3H functional group into SO_3^- functional group while deteriorating the electrocatalytic performance of the electrode too. We believe that -SO_3H functionalized MoS_2 nanosheets with expanded interlayer distance enhances the surface area, interfacial charge transfer kinetics, and H^+ adsorption-desorption by lowering the ΔG (energy barrier), enhancing the surface conductivity, and improving the catalytically active sites. The overpotential, Tafel slope, and R_{ct} were obtained as ~82 mV (η_{10}), ~57 mV/dec, and 0.69 Ω, respectively, along with excellent stability of 12 h for the SO_3H-MoS_2 (particularly for MoS_2-8), which are pretty close to equivalent Pt-wire. Using DFT, we calculated the work function for the pristine MoS_2 ~5.21 eV and -SO_3H functionalized MoS_2 ~4.82 eV. Such reduction in WF in SO_3H-MoS_2 indicates an increase in localized charge concentrations, which further improves the catalytic charge-transfer kinetics of such functionalized MoS_2 catalysts via Volmer-Heyrovsky mechanisms. We further believe that this work is unique, straightforward, and up-to-date, which will open a new paradigm of 2D-MoS_2 functionalizations, consequently paving pathways towards improving the catalytic activities of earth-abundant other 2D-TMDs for next-generation electrocatalysis.

Finally, chapter 6 presents the enhanced catalytic activity of sulfonic acid/sulfur trioxide (SO_3H/SO_3) functionalized 2D-MoS_2 nanosheets to degrade methylene blue dye. The SO_3H/SO_3-MoS_2 nanosheets were synthesized via hydrothermal method followed by structural and spectroscopic characterizations. Functionalization of 2D-MoS_2 was confirmed by Raman spectroscopy, FTIR, and XPS and found that the SO_3H/SO_3 molecules were covalently attached with the MoS_2 nanosheets. X-ray diffraction associated with SEM, HRTEM, and SAED illustrated that no significant changes occurred in the 2D-MoS_2, except the expansion of (002) interlayers of ~3.1 Å. The photocatalysis experiments show that the SO_3H/SO_3-MoS_2 exhibits enhanced activity of the redox reaction, which is primarily due to the widening of MoS_2 bandgap, enhanced surface area, introduction of a large amount of active catalytic sites, successively increased free electrons, and above all, the functional group attached to the MoS_2 nanosheets. The mechanism of faster rate kinetics in SO_3H/SO_3 -MoS_2 was elucidated and found that possibly various active oxygen species formed followed by light-driven charge transfer to the organic dye to degrade it. We believe that the expanded interlayer in SO_3H/SO_3-MoS_2 improves the ion diffusion kinetics in aqueous solution, increases surface area and catalytically active surface sites while reducing the diffusion barriers, thereby faster the light-driven charge transfer for the redox reaction. We believe that SO_3H/SO_3 functionalized 2D-MoS_2 with expanded interlayers could open up enormous possibilities of other 2D materials functionalization for wider applications, such as the removal of toxic pollutants, catalysis of organic molecules, heavy metal ions adsorption or removal, hydrogen evolution, enhanced redox process for electrochemical devices (psuedocapacitors, batteries), biomedical devices, and so on.

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7.2 Future scope of work

It is perceived that this works will open up a considerable amount of scopes to continue such nano-scale hetero-architecture developments by engineering their surface/interfaces, architecting their growth mechanisms, and constructing newer possibilities of a wide range of materials developments. In addition, this work will stimulate the inventions of many new paradigms of materials research, including processing, properties, structure-properties correlations, and applications. Finally, many new applications will be emerging related to electrocatalysis and photocatalysis for next-generations energy and environmental applications towards the building of a sustainable society. A detailed future scopes are listed as follows.

- ❖ It is essential to understand the role of interfaces of $MoNi_4/MoO_2$:rGO nanocomposite structures needs to be investigated to obtain more information regarding charge-transfer characteristics of the hetero-interface in order to improve the catalytic activity for water electrolysis.
- ❖ It is imperative to understand/study the growth mechanism of MoS_2 on $MoNi_4/MoO_2$ via the hydrothermal method as a function of time, followed by analyzing interface structure. It would be better to grow the nanohybrid structure directly over any metallic plate to improve the scalability.
- ❖ Direct growth of $MoNi_4/MoO_2$ nanostructures on rGO could provide a better interfacial charge transfer, thus, splitting water more effectively. Therefore, it is required to study some catalyst-assisted growth of $MoNi_4/MoO_2$ on rGO in order to achieve better interfacial properties.
- ❖ The synthesis/processing of sulfonic acid (SO_3H) functionalized 2D-MoS_2 nanosheets needs to be developed for pilot-scale to achieve scalability in next-scale.
- ❖ Also, it will be suggested to understand the mechanisms of transformations from SO_3H to SO_3 due to the precursor ratio change.

- It is advised to obtain some strategies for reusing functionalized MoS_2 for the photocatalytic application, thereby, separating out SO_3H/SO_3-MoS_2 from a solution seems to be highly challenging and need to be addressed with immediate effect.
- It is very required to investigate the real-time mechanisms of formation of superoxide anion radicals, (like, $O_2^{\bullet -}$ and $OH^{\bullet}$) for further designing the efficient photocatalytic systems.