Electrochemically Engineered Tungsten Disulfide and Phosphorene Quantum Dots for Electrocatalytic Applications

The discovery of Graphene paved the way to a brand-new scientific realm: Two-dimensional (2D) materials. Explicit research on graphene ignited the research on other 2D materials and we have now a wide spectrum of 2D materials of unique structural and electronic properties. One major reason for the search of other 2D materials is its intrinsic zero band gap which restricts them for optoelectronic applications. Consequently, 2D materials beyond graphene such as Transition Metal Dichalcogenides (TMDs, e.g. MoS2, WS2, MoSe2 and WSe2) and Phosphorene have emerged to tackle the bottlenecks associated with graphene. Band gap opening in 2D materials can be more realized by nano structuring TMDs and phosphorene to their quasi-0D quantum dots (QDs). Such a transformation presents constructive impacts as it endows enhanced quantum confinement effect and surface to volume ratio, ease of heteroatom doping and functionalization enabling them to be utilized for various applications such as electrocatalysis, bioimaging and optoelectronics. Though MoS2 QDs are explicitly studied as 'flagship' TMD QDs, limited abundance of Mo and its high industrial consumption necessitates the search of alternative TMDQDs. Therefore, WS2 QDs which resemble the lattice structure of MoS2 is a good alternative for MoS2 QDs. To date, the research progress in synthesizing WS2 QDs is mainly centred on liquid phase exfoliation (LPE). LPE has a major disadvantage of using high-boiling point solvent which presents destructive impact while separation. Similarly, phosphorene, single or few-layer of black phosphorus, was rediscovered in 2014 as a potential 2D material due to its remarkable performance in field effect transistors. Later, phosphorene QDs (PQDs) were first synthesized by LPE in 2015. These methods have their own limitations in terms of size tunability and choice of solvents. Therefore, synthesizing QDs from TMDs and Phosphorene is still in infancy and necessitates new synthetic approaches and studies on their properties.

Electrochemical synthesis of QDs from their bulk 2D bulk is a promising approach as it allows exact control of electrochemical behaviour at the electrode- VIII electrolyte interface and presents constructive impact by disrupting the van der Waals interaction between the layers. 'Customized QDs' can be obtained by tuning various factors such as electric field gradient and current across the electrode-electrolyte interface, nature of electrolyte, area of the electrode and anions/ cations offered by the supporting electrolyte. Factors such as duration of the experiment, temperature, dielectric constant and conductivity of the solvent also endow high degree of flexibility for electrochemical transformation. To be precise, tailor-made QDs (layer specific and size-tuned) for specific applications can be obtained by appropriate combination of applied potential, electrolyte and duration in an electrochemical synthesis. These are often a single step synthesis at room temperature which makes them industrially viable for obtaining QDs in bulk with large area electrodes. Towards this direction, this thesis contains six chapters, out of which four chapters discuss the electrochemical approach to synthesize WS2 and Phosphorene QDs from their bulk counterpart, their physicochemical properties and electrocatalytic applications**.**

Chapter 1 provides an overview of various aspects of 2D materials and their QDs. A thorough literature survey has been carried out to identify the present scenario of the existing approaches for WS2 & Phosphorene QDs synthesis and their limitations. A brief section of the chapter is dedicated to discuss some of the important properties and applications of TMDQDs and PQDs. Further, the characterization techniques adopted to study the physicochemical properties of the electrosynthesized QDs are also discussed.

Electrochemical exfoliation of 2D WS2 has not been explored aiming to understand the electric field induced morphological changes underwent by WS2.Towards this direction, **Chapter 2** presents the electrochemical synthesis of WS2 QDs from bulk WS2 and their enhanced electrocatalytic activity towards hydrogen evolution reaction than their bulk 2D form.

Deployment of the electrosynthesized QDs towards fabrication of various QDs based devices, necessitates development of methods to organize such QDs and a thorough understanding of their

stability when assembled onto a substrate. Accordingly, **Chapter 3** deals with the self-assembly of the electrosynthesized WS2 QDs onto a polycrystalline gold electrode and investigation of their adsorption kinetics. Changes in the open circuit voltage of the electrode were used as a key to monitor the adsorption. Further, thermodynamic parameters such as free energy of adsorption, enthalpy and entropy of adsorption are deduced using Langmuir model.

The next two chapters are centered on the electrochemical exfoliation of black phosphorus to yield blue luminescent PQDs. **Chapter 4** provides an understanding on the role of structural distortion and oxygen content in maintaining the structural integrity of electrosynthesized PQDs. The experimental findings are also complemented by the DFT calculations carried out on PQDs of various oxygen content.

Heteroatom doped QDs are anticipated to have altered electronic structure which can exhibit intriguing physicochemical properties. Accordingly, **Chapter 5** deals with the electrochemical preparation of nitrogen doped PQDs using nitrogen containing electrolyte such as acetonitrile with Tetraethylammonium tetrafluoroborate as supporting electrolyte. The products have about 3.8 at.% of nitrogen with nitrogen being present in two different chemical environments. Further the possibility to tune the electrochemical doping of nitrogen is demonstrated with appropriate combination of electrolyte and supporting electrolyte. The high quantum yield of the pristine and doped PQDs (83 and 88 %) could be utilized for light emitting devices.

The conclusions from the present work along with outlook are presented in **Chapter 6**.