

Preface

Energy conservation and environmental protection have remained an issue of great attention among scientific communities and climate activists from past decades. It has also stimulated the greater utilization of solar energy and renewables to bridge the gap between energy demand and energy consumption. Research efforts in the twenty-first century are directed more towards finding effective alternatives of fossil-based fuels in form of clean and renewable energy. At the same time, harnessing the solar power to drive the related reaction is of great significance to protect the Mother Nature from hazardous materials by their sensitive detection and selective remediation. Such necessities also come under the ambit of the sustainable development goals (SDGs) 6, 7, 13 and 14 set up by the United Nations General Assembly in 2015.

Deployment of H₂ as an energy carrier into fuel cells has acted as a promising milestone as it has a high energy density (120–142 MJ kg⁻¹). Hydrogen generation by electrocatalytic water splitting driven by renewable electricity is a promising pathway for the sustainable hydrogen economy as it also leads to less consumption of fossil-based fuels which in turn controls climate change. Noble metal platinum is still the best electrocatalyst for this purpose with a high exchange current density (j_0) and small Tafel slope, but its higher cost acts as a hindrance for commercial use. The research community is looking for an alternative of this precious metal, in this effort, transition metal-based carbide and carbon composites as an electrocatalyst and earth-abundant non-metal element-based materials viz. g-C₃N₄ are of great interest. Besides fossil-based fuels which emit greenhouse gas on combustion, there are many industrial pollutants and chemicals of carcinogenic nature such as azo dyes and phenolic compounds which are listed by the US

Environmental Protection Agency under the hazardous category for the environment. The sensitive detection and cost-effective removal of these anti-nature materials are part of the wide agenda of policy-making bodies at the global level.

The graphitic carbon nitride (g-C₃N₄) has drawn wide research interest owing to being a metal-free catalyst, easy to synthesize, stable to a range of acid-alkaline solution and its non-toxicity. The g-C₃N₄ is one of the oldest synthetic polymers having an N-rich framework and semiconductor features with a band gap value of 2.7 eV. It is visualized as a substitute for N-doped carbon composites.

The focus of the present thesis is to explore the electrocatalytic and photochemical features of the g-C₃N₄ and other carbon-based composites to address the energy issues and better environmental protection. We have focused our efforts on the functionalization of g-C₃N₄ with others semiconductor metal oxides, non-metal elements as well as carbon species that yield enhanced results via synergism.

The complete thesis work is divided into the seven chapters. The *Chapter 1* details about the graphitic carbon nitride, its history and synthesis process, dimensionality of g-C₃N₄ viz. zero-dimension, one dimension, two dimension and three-dimension, application areas of this 2D material and its limitation in bulk form. This chapter also talks about the various parameters of HER catalysts, charge storage features, photocatalytic features of g-C₃N₄ with other semiconducting metal oxide composites and appearance of fluorescent properties at zero dimension of carbon nitride viz. quantum dots. The *Chapter 2* covers concise details about the tools and instruments utilized for the characterization purpose of the as-synthesized samples as well as electrochemical instruments and related terminology. The *Chapter 3* explores the HER properties of nanocomposites prepared using various

weight % of red P immobilized over the rGO-g-C₃N₄ binary structure hydrothermally. This study sheds light on the exploration of earth-abundant metal-free element-based catalysts as an alternate for noble metal Pt. The **Chapter 4** is about the further exploration of transition metal-based carbides for the electrocatalytic HER properties by doping of heteroatoms Sulphur and nitrogen into the graphitic carbon encapsulation. The obtained results are significant in highlighting the role of heteroatoms for enhancing the active sites resulting in greater activity by the catalyst. The **Chapter 5** details the fluorescent sensing features of zero dimension of carbon nitride i.e., quantum dots. The S and O doped surface of carbon nitride quantum dots do detection of pollutant hydroquinone (H₂Q) by photoluminescence quenching via surface electron transfer. The **Chapter 6** again explores the photochemical properties of metal oxide-carbon nitride nanocomposites by photocatalytic dye degradation phenomenon. The optimal combination of semiconducting metal oxides Ag₂O and SnO₂ over the surface of g-C₃N₄ proves the most effective for the degradation of common textile azo dye under the sunlight as well as white light LED. The **Chapter 7** summarizes the complete research works and also highlights the space available to explore further viz. future scope in the work done so far.

The present thesis has compiled all the published results in *Electrochimica Acta* (2020 IF: 6.901), *ACS Energy & Fuels* (2020 IF: 3.605), *Spectrochimica Acta Part A* (2020 IF: 4.098), and *Materials Chemistry and Physics* (2020 IF: 4.094). ‘**Appendix B**’ covers the exploratory work of charge storage properties of g-C₃N₄ by structural modification and alkali metal doping at interlayers of g-C₃N₄.