INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
SHORT ABSTRACT OF THESIS

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Thesis Title: Optimizing Photocatalytic Hydrogen Evolution Through Synergistic Charge Transfer in Donor Acceptor Based Hybrid Photocatalyst

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SHORT ABSTRACT

Chapter 1 serves as a background for this thesis and as a basis for the works that are presented in the following chapters.

In **chapter 2**, role of oxygen content dependent RGOs in MAPI/RGO heterostructures has been investigated for photochemical and photoelectrochemical activities. This chapter also summarizes the fact that variation in extent of chemical reduction not only controls the atomic percentage of oxygen content, but also governs the varied bandgaps as well as band edge positions for three variants of RGOs. To rationalize the occurrence of disparities in photoelectrochemical and photocatalytic activities of all three MAPI/RGO composites, we have proposed an electron transfer mechanism, where depending upon the relative CBM positions of MAPI and respective RGO, dissimilar photogenerated electron transfer took place.

Chapter 3, summaries the role of solvent assisted morphology dependent MAPI for photocatalytic and photoelectrochemical activities. Altercation in reaction medium from HI to DMF not only alter the surface morphology from cuboid to rod shape, it also influences various aspects of photocatalytic and photoelectrochemical activities. $\mathrm{MAPI_{DMF}}$ exhibited superior performances in terms of HER activities by 28 times Compared to $\mathrm{MAPI_{HI}}$. The superior HER performances of $\mathrm{MAPI_{DMF}}$. To further boost the HER activity, a stable $\mathrm{MAPbI_3}$/polyfluorene composite was successfully prepared by an *in-situ* fabrication. The incorporation of polyfluorene on $\mathrm{MAPI_{DMF}}$ surfaces not only broadens the light absorption range but also enhances charge segregation and transport at the $\mathrm{MAPI_{DMF}/PF_{10}}$ interface, leading to improved photocatalytic and photoelectrochemical activities. Under optimized conditions, $\mathrm{MAPI_{DMF}/PF_{10}}$ exhibited a maximum HER activity of 6200 μmol h^{-1} g^{-1}.

Chapter 4 summarizes the influence of phosphorus doping on band gap and energy levels (CBM and VBM). This study elucidates that the band gap of MoS_2 declines from 1.39 eV for pristine MoS_2 to 1.28 eV for P50_MoS_2, and it further diminished to 1.07 eV for P100_MoS_2 upon doping with P. Concurrently, the VBM energy level of all the MoS_2 variants experienced a downward shift with increasing phosphorus doping. Consequently, P50_MoS_2/MABI and P100_MoS_2/MABI composites have established a type II heterojunction, whereas MoS_2/MABI results in a type I heterojunction. Despite of having type II heterojunction P100_MoS_2/MABI composites performed worst in terms of HER activity than others. P50_MoS_2/MABI demonstrated superior photocatalytic HER of 1176 μmol h^{-1} g^{-1} relative to the others.

Chapter 5 summarizes the chemical functionalization of g-C_3N_4 via a covalent methodology employing cyano porphyrin has been demonstrated to serve as a significant tactic for augmenting and introducing novel properties to g-C_3N_4, thereby facilitating charge separation and enhancing visible light absorption in the tail region of por_g-CN. This advancement enables the attainment of improved HER activities from ascorbic acid aqueous solutions. The covalent grafting of porphyrin moieties onto the g-CN sheet has provided coordination sites for transition metals such as Ni^{2+} and Co^{2+}. The presence of metalated porphyrin moieties on g-CN has been shown improved kinetics of photogenerated charge migration, as evidenced by photocurrent and impedance studies. Notably, the maximum hydrogen evolution recorded was 4200 μmol·$g^{-1}h^{-1}$, achieved by Co_por_g-CN.