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**Thesis Title:** Studies on Graphitic Carbon Nitride Nanostructures for Photovoltaic Applications.

### **Abstract**

Graphitic carbon nitride is a 2-dimensional material analogous to graphite. It possesses a layered structure consisting of triazine or heptazine motifs arranged in a hexagonal fashion. Owing to its layered structure, bonded via weak Vander Waals forces, it can delaminate the bulk material into graphene-like novel nanostructures (nanosheets and quantum dots). It possesses promising material properties such as n-type semiconducting nature, strong absorption in UV-visible region, high chemical stability, and tunable optoelectronic properties making it a potential candidate for optoelectronic device applications. Herein, we have demonstrated the facile synthesis strategy to synthesize g-C<sub>3</sub>N<sub>4</sub> nanosheets (NS) and quantum dots (QDs) by green route using water as the exfoliating agent and chemical acidification of bulk material followed by hydrothermal treatment, respectively. The structural and optical properties were investigated in detail to understand the structure-property relationship of prepared low-dimensional materials. It was observed that chemical structure was well preserved even after exfoliation and acidification of bulk material into nanosheets and quantum dots. The NS and QDs possess an ultra-thin nature as evident by AFM and HRTEM images having thicknesses below 5 nm and 1.7 nm, respectively. These nanostructures possess tunability in optical properties as observed from blue-shifted absorption and emission spectra. Moreover, a reduction in Urbach energy after exfoliation suggests a smaller probability of photogenerated carrier recombination. These appealing properties pave the path for the

utilization of these nanostructures for photovoltaic applications either as an additive for the active/interface layer or as a charge selective layer.

The multi-functionality of the prepared quantum dots was explored as an additive for poly(3-hexylthiophene-2,5-diyl):[6,6]-phenyl-C71-butyric acid methyl ester (P3HT:PC<sub>71</sub>BM) blend active layer. The QDs were prepared in organic solvent (o-dichlorobenzene) to maintain compatibility with the device fabrication process. The photovoltaic effect formation and various effects of g-C<sub>3</sub>N<sub>4</sub> QDs on energy transfer, carrier transport, and nanoscale morphology were investigated in detail by incorporation as a third component into a well-established material combination of P3HT:PC<sub>71</sub>BM blend films. The emission spectra of g-C<sub>3</sub>N<sub>4</sub> QDs and absorption spectra of P3HT were found to have overlapping features that enabled the QDs to transfer ultraviolet region photons to P3HT. The g-C<sub>3</sub>N<sub>4</sub> QDs were found to assist Förster resonance energy transfer (FRET) between the QDs and host polymer, improving the overall energy harvesting capability of the devices. Moreover, g-C<sub>3</sub>N<sub>4</sub> QDs were favorable in maintaining nanoscale phase segregation of the active layer with improved crystallinity which is crucial for efficient exciton dissociation and faster charge extraction. Incorporation of g-C<sub>3</sub>N<sub>4</sub> QDs, improved the device efficiency by almost 40% for optimal concentration of QDs i.e. 2 Vol% compared to reference one. The improved device efficiency is thus attributed to the combined consequences of improved morphology and the FRET effect.

The g-C<sub>3</sub>N<sub>4</sub> NS and QDs were utilized as a secondary dopant to modulate the structural and electronic properties of commonly used hole transport layer viz. PEDOT:PSS. The addition of NS and QDs weakened the columbic interaction between the PEDOT and PSS leading to the formation of an expanded coil-like structure. This resulted in the reorientation of the PEDOT chain forming the interconnected charge transport pathways thereby, improving the conductivity of modified films. When employed as a hole transport layer in polymer solar cells they yielded the power conversion efficiency of 7.65% and 6.44% at an optimal concentration

of 50 Vol% and 60 Vol% for NS and QDs, respectively, compared to 5.45% for reference one. This improvement in photovoltaic performance can be attributed to the increased short circuit current density ( $J_{SC}$ ), charge carrier mobility, fill factor (FF), and reduced series resistance ( $R_s$ ). However, the FF was higher for NS-based devices as they provide better continuous charge hopping pathways compared to QDs. Moreover, the modification in the molecular structure of PEDOT:PSS via NS and QDs resulted in improved device stability compared to reference one, retaining almost 40% of initial power conversion efficiency even after 200 min of continuous illumination. These results demonstrate the systematic strategy for improving the conductivity and mobility of HTL resulting in efficient extraction of charge carriers and enhanced device performance and stability.

The g- $C_3N_4$  NS was utilized as a charge selective layer in polymer solar cells both for extraction of electrons and holes. The work function of ITO decreased from 4.94 eV to 4.43 after coating with NS. However, with UV-Ozone treatment gradual increase in work function was observed and for the optimal treatment duration (10 min), it reaches 5.24 eV. This suggests that in its pristine form, i.e. untreated ITO/ g- $C_3N_4$  NS, it can extract electrons and therefore can be utilized as the cathode interface layer for inverted solar cells while after UV- $O_3$  treatment it facilitates the extraction of holes and thereby can be used as an anode interface layer in conventional device architecture. This has been demonstrated with the active layer combination of PTB7-Th:PC<sub>71</sub>BM. Similar short circuit current densities (15.65 mA cm<sup>-2</sup>) and power conversion efficiencies (5.60% and 6.05%) were observed for both inverted and conventional devices having g- $C_3N_4$  NS as the charge selective interface layer. The UV- $O_3$  treatment seems to modify the g- $C_3N_4$  NS thin film by inducing surface dipoles due to the incorporation of oxygen atoms which is primarily responsible for their switching work function as observed. This study demonstrates the dual functionality of g- $C_3N_4$  NS as a charge selective interface layer (CIL/AIL) for solution processable polymer solar cells.

The  $g\text{-C}_3\text{N}_4$  possesses unique optoelectronic properties, however, its thin-film characteristics were not well explored, therefore, limiting its utilization for semiconductor device applications. Herein, we fabricated the thin film of 10 nm via thermal evaporation and studied the effect of UV- $\text{O}_3$  treatment on structural, optical, electrical, and dielectric properties. Systematic improvements in film characteristics were observed until 10 min treatment duration. However, a further increase in treatment duration resulted in a detrimental effect on the thin-film properties. It was observed that structure was well retained for the thin film after thermal evaporation and UV- $\text{O}_3$  treatment, as that of bulk  $g\text{-C}_3\text{N}_4$ . Moreover, the thermally evaporated film exhibited a smooth surface with r.m.s roughness well below 1 nm and the smoothness of the film further increased after treatment. The emission properties and Urbach energy analysis suggested reduced charge carrier recombination leading to better photo-induced charge separation in thin film after UV- $\text{O}_3$  treatment. The treated thin film exhibited a smaller leakage current resulting in a higher dielectric constant and smaller loss.

All the above results suggest that  $g\text{-C}_3\text{N}_4$  nanostructures and thin film possess appealing structural, optical, and electrical properties which can significantly improve the performance of polymer solar cells. However, its several unique features pave the path towards utilization in other semiconductor devices too, like perovskite solar cells, light emitting diodes, photodetectors, wearable sensors, energy storage devices etc.