Abstract:

Nitrogen-doped carbon dots (NCDs) have emerged as versatile carbon-based nanomaterials owing to their tunable structural domains, rich surface functionalities, unique photophysical properties, and promising catalytic potential. The present thesis systematically investigates the temperature-dependent structural evolution of NCDs synthesized via a solvent-free, one-pot thermal pyrolysis of citric acid and urea, and correlates these structural transformations with their multifunctional performance in heterogeneous catalysis, electrocatalysis, and fluorescence-based sensing.

NCDs were synthesized at different carbonization temperatures (140–400 °C), enabling controlled modulation of their structural domains from hydrogen-bonded molecular clusters to disordered and subsequently graphitic carbon frameworks. Comprehensive structural, spectroscopic, and microscopic characterization revealed that lower synthesis temperatures favour molecular-domain-rich structures with abundant surface functional groups (–NH_2, –OH, –CONH–), whereas higher temperatures promote graphitic core formation accompanied by changes in nitrogen bonding configurations and defect density.

The molecular domain-rich NCD140 demonstrated superior heterogeneous base catalytic activity in model Knoevenagel–Doebner and Aldol condensation reactions, achieving 75% and 71% conversion, respectively. The enhanced catalytic efficiency was attributed to surface Lewis basic sites, particularly amine functionalities that facilitate proton abstraction and carbon–carbon bond formation. In contrast, increased carbonization at 300 °C resulted in reduced surface basicity and diminished catalytic performance, establishing a clear structure–activity relationship and positioning NCDs as sustainable alternatives to conventional metal-based base catalysts.

Electrocatalytic studies revealed a temperature-driven modulation of catalytic selectivity between the CO_2 reduction reaction (CO_2ER) and the hydrogen evolution reaction (HER). NCD3 (300 °C) exhibited the highest CO_2ER performance with a Faradaic efficiency of ~69.96% and a current density of 4.3 mA cm^{-2}, producing methanol, acetate, and n-propanol. The enhanced activity was correlated with optimized disordered graphitic domains and abundant pyridinic nitrogen species, facilitating efficient charge transfer. Conversely, NCD4 (400 °C) favoured HER, highlighting how nitrogen configuration and defect structures dictate catalytic pathway selectivity.

The thesis further elucidates the molecular origin of fluorescence in dual-emissive (NCD1) and single-emissive (NCD2) systems synthesized at 140 °C and 240 °C, respectively. The transition from molecular fluorophore clusters to amorphous carbon nanodots significantly influences emission behaviour and sensing mechanisms. Fluorescence-based detection of bilirubin (BR) and Cu^{2+} ions demonstrated distinct quenching pathways governed by structural domains. BR detection using NCD1 proceeds *via* ground-state complex formation (static quenching), while NCD2 follows an inner filter effect (IFE) mechanism. Cu^{2+} sensing for both systems occurs through electron transfer (dynamic quenching). The differing limits of detection and quenching mechanisms establish clear structure–property–function correlations.

Overall, the thesis demonstrates that solvent-free thermal pyrolysis serves not merely as a synthetic route but as a controllable parameter for engineering domain architecture in nitrogen-doped carbon dots. By integrating heterogeneous organocatalysis, electrocatalysis, and fluorescence sensing within a unified structural framework, this work advances fundamental understanding of temperature-mediated structural tuning and establishes NCDs as multifunctional, sustainable nanomaterials for catalytic and sensing applications.

Keywords: *Nitrogen doped carbon dots (NCDs), molecular fluorophores, graphitic domain, carbon nanodots, Knoevenagel-Doebner Condensation, Aldol Condensation , Electrocatalytic CO_2 reduction, Hydrogen evolution reaction, sensing, static quenching, IFE, photoinduced electron transfer, Cu^{2+} ions, bilirubin.*