Thermal and Kinetic Evolution of Boron, Phenyl Co-Doping in a Triazine Network

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In the recent decades, carbon nitrides have shown great promise as semiconductor materials in a variety of applications, from solar fuels production, bio-imaging, sensing, light-emitting diodes to solar cells. Their structural, electronic, and optical properties, along with their low price, environment-friendly nature, and high chemical serve as great advantages. [1] Recently, phenyl-modified carbon nitride (PhCN) has evolved as an advanced carbon nitride material analog, with a higher visible-light absorption and warm LED applications.[2], [3] This modified carbon nitride exhibits remarkable optical properties arising from extended π conjugation due to the presence of phenyl groups. Its easy synthesis, with only one precursor- 2,4-diamino-6-phenyl-1,3,5-triazine (DPT) through thermal polymerization process at around 400 °C, poses additional advantage for scalability.[4], [5] The low polymerization temperature results in low defect density and high photoluminescence and a quantum yield (PLQY) (above 40%). PhCN has been widely used for lighting and bioimaging applications, and photocatalysis under visible-light irradiation.[6] It has been reported that the conjugation degree of the PhCN polymer influences its main optical properties. A study of the intermediates formed while preparing PhCN showed the correlation between the structure and optical properties.[7]

Doping is a well-established method in semiconductor science to modify and enhance material properties. In the case of carbon nitrides, elemental doping is widely explored to overcome limitations such as low visible-light absorption and rapid electron-hole recombination.[8] Non-metal doping introduces defect sites and modifies the band structure, which can lead to improved visible-light absorption and more efficient charge carrier separation without significantly affecting the stability of the carbon nitride framework. [9]This metal-free approach is particularly attractive for sustainability goals as they do not possess reactive sites like metal atoms, would not lead to eutrophication and have higher stability when compared to metal-doped counterparts. Many reports have arose stating the benefit of Boron incorporation in g-C_3N_4 matrix utilizing it for all sorts of g-C_3N_4 applications like- CO_2 reduction, organic pollutant degradation, water splitting, photoluminescence, electroluminescence, H_2O_2 synthesis, pharmaceutical degradation and more.[8], [9], [10], [11], [12]

Herein, we dope Boron atoms into the phenyl-triazine matrix of the PhCN precursor– 2,4-diamino-6-phenyl-1,3,5-triazine (DPT) through thermal copolymerization with boric acid (BA) to obtain a boron-doped phenyl-modified carbon nitride (BPhCN) structure. A detailed synthetic study was conducted by investigating the intermediates formed at different temperatures and treatment times. This thermal and kinetic evolution of the polymerization mechanism of BPhCN was studied through X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron (XPS) spectroscopy and Photoluminescence (PL) mapping and compared to that of PhCN. Figure 1depicts the difference in the thermal evolution of the two different polymers-BPhCN and PhCN under same conditions.

The detailed investigation shows that the introduction of B atoms in high amounts slows down the process of formation of heptazine rings at a lower temperature, increases the crystallinity of the material and introduces multiple defect-states. The same ratio of B:CN showed a tuneable optical emission dependent on the treatment duration, where a sharp blue emission was observed by the highly crystalline dimer phase and a broad red-edge effect was observed for the semi-crystalline graphitic phase. The results show a promising future for BPhCN materials in LED, bio-imaging and sensor applications.

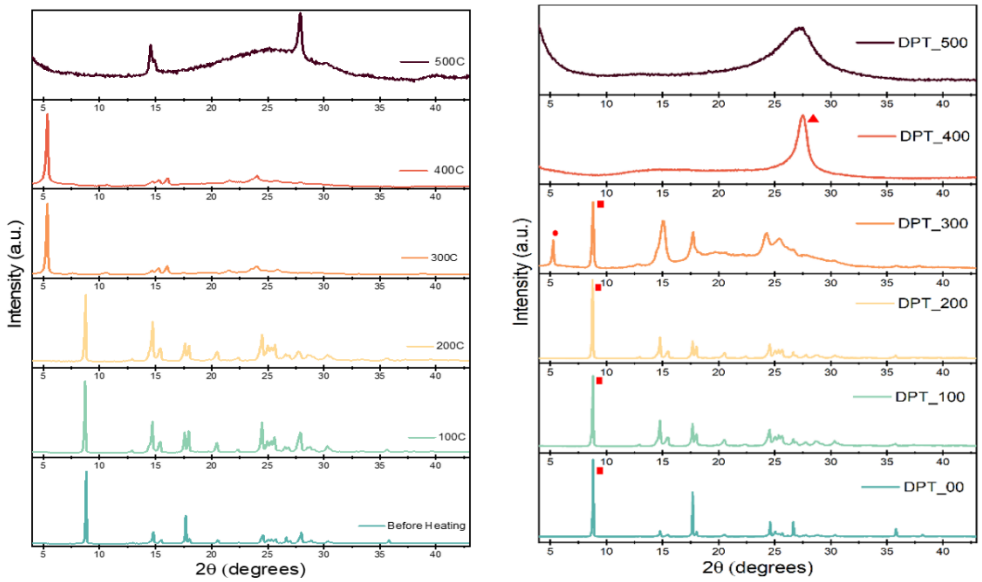

Figure 1 – Thermal evolution of the polymer a) BPhCN compared to b)PhCN.

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