SYNTHESIS, PHOTOPHYSICAL STUDIES AND CHEMICAL SENSOR APPLICATIONS OF LUMINESCENT CARBON DOTS

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by

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ABSTRACT

Over past two decades, there has been an intense focus to understand and to extend the technological boundaries of carbon-based nanomaterials such as graphene, carbon nanotubes, fullerene, graphene quantum dots, and carbon dots (CDs). Among these, due to their bright fluorescence, tuneable luminescence, facile synthetic routes, CDs have captivated the attention of fluorescence community. CDs can overcome the toxicity associated with semiconductor-based fluorescence quantum dots (QDs) and photobleaching tendency of organic fluorescent dyes. There has been an enormous number of publications emphasizing both fundamentals and technological aspects of CDs. Despite there is an excellent progress, the fundamentals of photophysics are not evident in CDs. The predominance in blue emission and the weak solubility in the non-polar environment are the various aspects needs to be addressed. Although there was a substantial number of applications, where CDs have scrutinized, there is still room for exploration. We have synthesised a range of CDs, studied the photophysical properties and demonstrated its chemical sensor applications for the detection of biological, environmental and industrially significant molecules/ions. The studies conducted using various CDs given in this Thesis is briefed below.

Ammonia is an important industrial gas and it has a biological and environmental significance. A fluorescent-based probe, which operates via Forster Resonance Energy Transfer (FRET) mechanism explored for the ammonia detection in gaseous as well as the liquid state using CDs as a fluorophore. The CDs, derived from carbonizing acetic acid and sodium rhodizonate was used as the sensor system. CDs acted as a signal transducer and sodium rhodizonate as an analyte-specific molecule. Both solution and vapor phase detection of ammonia was performed. Excited state energy transfer (FRET) from CDs to sodium rhodizonate was activated when ammonia was present in the sensor solution. The detection limit of the current sensor system was 3 ppm. Selectivity was demonstrated using oxides of nitrogen and common organic solvents.

A nitrogen-rich carbon dots (NCDs) having broad emission covering a substantial portion of visible regions (nearly white light) of the electromagnetic spectrum was synthesized using ethylenediamine as carbon and nitrogen precursor. An attempt to understand the broad emission from NCDs was performed by interacting with Cu^{2+}. The detailed spectroscopic and microscopic studies reveal that the broad, steady-state photoluminescence emission of NCDs originates from the direct recombination of excitons (higher energy) as well as due to the involvement of defect states (lower energy). A selective fluorescence platform for the detection of Cu^{2+} using NCDs was also accomplished. The detection limit was 10 μM and the dynamic range was 10 μM – 0.4 mM.

A hydrothermal synthetic route for a bright blue emitting silicon passivated carbon dots gel (SiCDs gel) was accomplished using an aminosilane precursor. A detailed microscopic, spectroscopic, rheological and surface area analysis confirms that the CDs attached to the polymeric backbone. Nitrogen adsorption studies shows that the gel has high nitrogen adsorption tendency, approximately two orders of magnitude higher than that of the conventional CDs. A fluorescence sensor for

Ag^+ ions using SiCDs gel, which operates via the formation of Ag nanoparticles on the SiCDs gel surface, was demonstrated. The luminescence of CDs was quenched by Ag nanoparticles formed on the surface, which was proportional to the concentration of Ag^+ ions. The sensor shows high selectivity towards Ag^+ with a sensitivity and dynamic range of 85 nM and 0.4 μM – 0.1 M, respectively.

Hydrothermal synthesis of sulfur and nitrogen doped carbon dots referred as 'SNCDs' was achieved using glutathione as a single precursor of carbon and dopants. The reason behind atypical fluorescence emission profile of SNCDs, showing both excitation dependency and independency unfolded by comprehensive pH-dependent fluorescence studies. Based on the results, a complete energy level diagram of SNCDs was proposed. Further, SNCDs was utilized for selective detection of Cr(VI), which operates via both FRET and inner filter effect (IFE).

CDs having high solubility in non-polar environment referred as 'organophilic CDs (OCDs)' was synthesized using cyclohexane as a precursor and dispersion media. Spectroscopic studies revealed the presence of non-polar functional groups at the OCDs surface. OCDs was then utilized for nitroaromatics sensing. The fluorophore was found to be highly sensitive to trinitrophenol (TNP), compared to the other nitroaromatics, in turn opening up the possibility of detection of potent explosives and environmental pollutants. An attempt to understand the mechanism of fluorescence quenching of OCDs by nitroaromatics was made. OCDs' emission was quenched by primary inner filter effect (IFE), which happens by the absorption of nitroaromatics at the excitation wavelength of OCDs, against commonly observed electron transfer mechanisms.

We envisage that the studies presented here would be highly useful in understanding the properties of CDs in depth and to extend its technological realms by encouraging the possibility of various synthetic routes and applications.