

Abstract

Carbon's remarkable ability to form small as well as long chain structures, and its dexterity to exist in various allotropic forms, is the foundation of its propensity to produce new materials and/or generate a variety of nanostructures with fascinating properties. Such nanostructures, with the central core being exclusively composed of carbon atoms, can be classified as carbon – based nanostructured materials (CNMs). One of the recent additions to the CNMs family, that has attracted a great deal of attention because of their unique properties, are the zero dimensional fluorescent carbon dots (or, graphene quantum dots, carbon quantum dots). They have a core composed of graphite sheets while the external shell could be decorated with a range of functional groups, depending on the type of precursors used and the methodology followed for their synthesis.

Literature reports several methods of synthesis of carbon quantum dots (CDs) using a variety of starting materials however, investigation into their structural detail is rare or sporadic. The research presented in this thesis will therefore attempt to establish a versatile, one-pot solution-based methodology for the preparation of CDs and to decipher their chemical structure. The chemical structure determination studies of the fluorophore envisioned the presence of pyridine-carboxylic acid moieties and their derivatives.

Further, amplification of the fluorescence quantum yield of the CDs through surface conjugation with electron rich heteroatoms has been documented in literature nevertheless, there is still scope to systematically study the effects of various heteroatoms present on the CD–surface and explore their potential technological relevance. Accordingly, the present research endeavours to investigate the (i) nitrogen doped CDs (i.e., N–CDs) and (ii) nitrogen and sulphur co-doped CDs (i.e., N, S–CDs), and examine their prospect as efficient fluorescent probes in the detection of picric acid and, Hg (II) & thiourea in aqueous solution. Herein, quenching of the fluorescence intensity of the N–CDs in presence of picric acid, attributed to the electron transfer and energy transfer processes, has been collated to the measure of picric acid in aqueous samples and the detection limit (LOD) is estimated to be 33 nM. Analogously, N, S–CDs have established as a proficient fluorescent turn – off – on probe for rapid and selective detection of the toxic heavy metal ions, Hg (II), and Thiourea in aqueous solution with the detection limit of 6.9 nM and 240 nM respectively

The physicochemical properties (such as – thermal, electrical, electrochemical, optical, biological and so forth) of carbon nanostructures are excellent by themselves yet, it has been recognised that their hybrid nanomaterials (HNMs), devised by combining with other nanostructured materials, could be engineered to accomplish desired combination of functionalities through a synergistic relationship. Working in line with this theme, the present thesis also undertakes the formulation of two carbon – based hybrid nanostructured materials (CHNMs) comprising of (i) Nitrogen and sulphur co-doped CDs and gold nanoparticles (i.e., the N, S–CDs – Au HNMs) and (ii) Graphene oxide (GO) and CuO nanostructures of various morphologies [such as – spherical (i.e., CuOA – GO HNMs), rods (i.e., CuOW – GO HNMs), star (i.e., CuOC – GO HNMs), and flower (i.e., CuOT – GO HNMs)], and attempts to assess their catalytic performance compared to the respective free metal (i.e., Au) or metal oxide (i.e., CuO) in the reduction of 4- nitrophenol (4–NP) in presence of excess of sodium borohydride (NaBH₄). Studies reveal N, S–CDs–Au HNMs could accomplish one of the highest values of apparent rate constant reported in the literature so far ($k_{app} = 1.37 \times 10^{-1} \text{ s}^{-1}$) thereby, validating their superior catalytic efficacy compared to Au nanoparticles. Similarly, the different CuO – GO HNMs were found to exhibit better catalytic ability, in the reduction of 4-NP, compared to their respective CuO morphologies, possibly due to synergetic relationship between the CuO nanostructures and GO. In addition, CuOA – GO HNMs (i.e., formulation comprising of spherical shaped CuO nanostructures) are found to have the highest values of apparent rate constants (k_{app} ; $4.90 \times 10^{-3} \text{ s}^{-1}$) and Turnover Frequency (TOF; $980 \text{ g}^{-1}, \text{ s}^{-1}$) compared to the other hybrid formulations with rod–, flower–, and star shaped CuO nanostructures owing to their smaller particle size, spherical shape and better distribution over GO surface.

Keywords: Hybrid nanomaterials, Carbon dots, Detection limit, Cupric oxide, 4–Nitrophenol.