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Strongly blue-luminescent N-doped carbogenic dots as a tracer metal sensing probe in aqueous medium and its potential activity towards *in situ* Ag-nanoparticle synthesis

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ABSTRACT

Milligram scale one-pot synthesis of N-doped, blue luminescent, highly water soluble and short fluorescent lifetime carbogenic dots have been developed by thermal coupling of tris(hydroxymethyl)aminomethane (tris) and glycine. The size distribution is in the range of 1.5-4.5 nm with a high abundance of 3 nm particles. The atomic force microscopy (AFM) also confirms the TEM particle size data. The carbogenic dots show pH sensitive and excellent saline environment stability without diminishing major fluorescent character. The nitrogen doped carbon dots (NCDs) can anchor Cu^{2+} ions in aqueous solution which results major drop off effect in fluorescence intensity by inner filter effect. Our as prepared CDs have a unique ability to detect Cu^{2+} ion with a detection limit of 0.32 μM in the dynamic range of 0.4–300 μM. The prepared carbon dots have also showed potential activity as a reducing agent. Here, silver nanoparticles have been synthesized without using any external rigorous reducing agent or conditions. Meanwhile our synthesis was also less time consuming and the derived carbon dots can also stabilize the nanoparticles without agglomeration up to several weeks.

1. Introduction

Fluorescent carbogenicdots (often called carbon quantum dots or C-dots), an emerging member belongs to carbon nanomaterial community, were first obtained as sludge during refining of single-walled carbon nanotubes in 2004 and via laser ablation of graphite powder and cement in 2006 [1,2]. Carbon dots are nanomaterials of carbon family with a size of less than 10 nm [3]. These are basically physiologically benign and inexpensive materials which ensued in various applications in biological leveling, optoelectronics, potential catalytic technology and biomedicines [4–10]. Photoluminescent carbon dots are superior to traditional semiconductor carbon dots and organic dyes in the area of water solubility, functionality and relatively high quantum yields. Photoluminescent carbon dots are superior to traditional semiconductor carbon dots and organic dyes in the area of water solubility, functionality and relatively high quantum yields [11]. Water solubilization of carbon as nanodots exhibits strong luminescence for which they are addressed as carbon nanolights [12–14]. Many researchers developed many routes to form carbon dots like high energy ion beam radiation and laser ablation techniques [15]. But one major drawback for these techniques is all are expensive, energy intensive. To minimize such problems relatively low cost, different chemical methods were adapted to synthesize carbon dots. Acid oxidized gas shoot or activated carbon, oxidized candle shoot were used to develop carbon dots in a low cost [16,17]. Carbon dots from green source are also practiced immensely due to abundant source, low cost and water solubility. De et al. developed banana leaf based extract for preparing carbon dots [18]. Other viable natural sources were used for carbon dots synthesis with improved luminescent property [19–22]. Carbonization of glucose, sucrose, diols, triols, ascorbic acid, amino acids etc. has also attained substantial attention for the production of fluorescent carbon dots. But maximum processes demand multistep operations or strong acid treatment followed by using of surface passivation agents [23–26].

In very recent era, fluorescent carbon dots have played as chemosensors for the detection of heavy metal ions, even at as a tracer element. These carbon dots have significant intrinsic sen-

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sitivity, chemoselectivity towards metal ions, rapid detection and real time monitoring propensity [27–38]. Copper ion plays a significant role in chemical, environmental and biological systems. It is also an essential element for animals and humans in trace amount [39]. But according to U.S. environmental protection agency (EPA), it becomes toxic if the permissible level in water is above 1.3 ppm or approx. 20 μM [40]. The tolerance limit of copper ion (+2) in human blood is 15.7-23.6 μM [41]. But above the permissible level of the Cu^{2+} ion in blood causes gastrointestinal disturbance or severe liver and kidney damage upon prolonged exposure [29]. There are several methods also used to detect Cu^{2+} ions, viz. atomic absorption spectroscopy[42], inductively coupled mass spectroscopy [43] and electrochemical methods [44]. But the main drawback in such methods are that, these are highly expensive, sophisticated and sometimes time consuming also. Hence, to qualify and quantify the Cu^{2+} ion in environment and ecosystem, analytical methods to sense Cu^{2+} ion become very desirable. There are many fluorescent sensing probes already have been published for sensing of copper ion (+2), such as organic dye or organic complex [45–48], carbogenic dots [49], inorganic quantum dots [50], etc. In this context it is highly worthy to detect heavy metal ions in aqueous medium with low cost and rapid-sensing of Cu^{2+} ions in biological, environmental and toxicological samples with avoiding of those aforementioned difficulties.

Herein, a single-step eloquent approached has been developed to prepare N-doped carbon dots (NCDs) with blue emitting fluorescence. The fluorescence activity was quenched by several metals ions, but a drastic quenching was occurred in presence of Cu^{2+} ions. This attempt might provide a new pathway in Cu^{2+} ion detection also in tracer amount in aqueous medium.

2. Experimental details

2.1. Materials

Glycine and tris(hydroxymethyl)aminomethane (tris) were purchased from Sigma Aldrich. Phenol, methanol and hydrogen peroxide was procured from Merck, India. All chemicals used here were reagent grades.

2.2. Synthesis of tris-glycine carbon dots (TG-CDs)

Tris-glycine C-dots were synthesized by thermal coupling of tris(hydroxymethyl)aminomethane i.e. tris and glycine. Initially 1 g of glycine (13.32 mmol) mixed with equivalent amount of tris aqueous solution (2 mL). Then the solution was evaporated to dryness at 220 °C in a muffle furnace. A sticky brownish mass was obtained after water evaporation after drying it at 80 °C for 72 h. The solid mass was crushed into fine powder and extracted with hot water. The supernatant was collected after centrifuged it at 12000 rpm for 30 min. The solvent was evaporated again from the solution at room temperature under vacuum to obtain fluorescent C-dots with mass yield of 54%.

2.3. Catalytic reduction to prepare silver nanoparticles (AgNPs)

To prepare AgNPs, an aqueous solution of silver nitrate ($AgNO_3$) having concentration of 8×10^{-2} mol L^{-1} was incubated with C −dot aqueous dispersion (35 mg L^{-1}), and NaOH (0.01 M) in 50 °C in a water bath for 5 min. The acidity of the mixture was maintained at pH = 4 for the uniform growth of AgNPs.

2.4. Characterization

The FTIR spectrum of C-dots was performed on a FTIR spectrophotometer (Perkin Elmer, model-Spectrum-2, Singapore) using KBr pellet made by mixing KBr with fine powder of the C-dots (10:1 wt ratio of KBr to C-dots). Each FTIR spectrum was scanned with a resolution of 4 cm^{-1} and 16 scans in the wavelength range of 500−4000 cm^{-1} at room temperature. The elemental composition was determined electron dispersive X-ray study (EDX, INCA PentaFET x3, Oxford Instrument UK). X-ray diffraction (XRD) experiment was performed in Bruker, D2 phaser with SSD160 detector. The morphology and the microstructure were evaluated by high resolution transmission electron microscope, HRTEM (JEOL, Japan operating voltage 200 kV with filament LaB_6). Surface topography of TG-CDs was scanned by Agilent 5500 scanning probe microscope (resonance frequency of tip is 146–236 kHz and force constant was kept at 48 Nm^{-1}) after drop casting of TG-CDs on Silicon wafer as substrate. The images were taken in non-contact tapping mode with a scan area of 500×500 nm^2. Raman measurement was measured using spectrometer (MODEL T64000 (Make JobinYvon Horiba, France). Argon-Krypton mixed ion gas laser (MODEL 2018 RM) was used as an excitation source. Thermoelectric cooled front illuminated 1024 256 CCD, MODEL Synpse TM (Make JobinYvon Horiba, France) was used as the detector. The X-ray photoelectron spectra have been performed in PHI 5000 Versa Probe II scanning X-ray photoelectron spectrometer (XPS), with a monochromatic Al K_α source (1486 eV). A UV–vis spectrum of C-dots in aqueous solution was recorded using UV–vis spectrophotometer (Perkin Elmer, Singapore PTE Ltd., Model lambda 35). The zeta potential was recorded on a Zetasizer Nano ZS90 (Malvern Instruments, Manchester, U.K.) Fluorescence measurements and resonance light scattering were analyzed on a Fluoromax_4C_1052D_4312_FM spectrofluorometer in aqueous solution. The fluorescence lifetime was carried out on a time-resolved fluorescence spectrometer FL3-P-TCSPC (Horiba Jobin Jvon, France).The quantum yield of C-dots were calculated at an excitation wavelength of 350 nm by the equation given below [51],

$$Q_{CD} = Q_R . \frac{I_{CD}}{I_R} . \frac{A_R}{A_{CD}} . \frac{\eta_{CD}^2}{\eta_R^2} \quad (1)$$

Where 'Q' represents the quantum yield, 'I' is the intensity of luminescent spectra, 'A' is the absorbance at particular exited wavelength and 'η' is the refractive index of the solvent used. Here, in our study we have chosen quinine sulfate in 0.1 M H_2SO_4 as standard and its quantum yield (Q_{CD}) is known to be 54% in 0.1 M H_2SO_4 solution. The subscripts 'CD' for C-dots and 'R' for reference are used in this equation.

3. Results and discussion

3.1. Characterization of tris-glycine C-dots

A simple approach for the preparation of single step photoluminescent water soluble NCDs from organic precursors, like 2-amino-2-hydroxymethylpropane-1, 3-diol (tris) and glycine (gly) has been developed and presented in Scheme 1. The tris part played as the carbon source and the glycine moiety was acted as surface functionality. Glycine was attached to the exterior surface of the nanoparticles through amide linkages imprinted *in situ* by thermal condensation among the ammonium carboxylate groups (viz. $-NH_3^{+-}OOC- \rightarrow -NHCO- + H_2O$) [52]. Zeta potential of the C-dots was found to be −20.8 mV which confirmed the formation of highly stable anionic type C-dots. Using quinine sulfate in 0.1 M H_2SO_4 as a reference, the quantum yield value was calculated to be 42%.

The formation of C-dots having a major abundance of 3 nm in average size was confirmed from HRTEM micrographs as shown in Fig. 1(a-c). The HRTEM images clearly disclose that all C-dots are spherical in shape with a narrow size distribution in the domain