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Zinc and nitrogen ornamented bluish white luminescent carbon dots for engrossing bacteriostatic activity and Fenton based bio-sensor

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ABSTRACT

Carbon dots with heteroatom co-doping associated with consummate luminescence features are of acute interest in diverse applications such as biomolecule markers, chemical sensing, photovoltaic, and trace element detection. Herein, we demonstrate a straightforward, highly efficient hydrothermal dehydration technique to synthesize zinc and nitrogen co-doped multifunctional carbon dots (N, Zn-CDs) with superior quantum yield (50.8%). The luminescence property of the carbon dots can be tuned by regulating precursor ratio and surface oxidation states in the carbon dots. A unique attribution of the as-prepared carbon dots is the high monodispersity and robust excitation-independent emission behavior that is stable in enormously reactive environment and over a wide range of pH. These N, Zn-CDs unveils captivating bacteriostatic activity against gram-negative bacteria *Escherichia coli*. Furthermore, the excellent luminescence properties of these carbon dots were applied as a platform of sensitive biosensor for the detection of hydrogen peroxide. Under optimized conditions, these N, Zn-CDs reveals high sensitivity over a broad range of concentrations with an ultra-low limit of detection (LOD) indicating their pronounced prospective as a fluorescent probe for chemical sensing. Overall, the experimental outcomes propose that these zero-dimensional nano-dots could be developed as bacteriostatic agents to control and prevent the persistence and spreading of bacterial infections and as a fluorescent probe for hydrogen peroxide detection.

1. Introduction

In recent era, with the astonishing advances of nanotechnology, nanoparticles with distinct physical and chemical properties have revealed an increasing significance in biomedical, biological, and pharmaceutical applications [1,2]. Owing to the advancement in science and technology it has become possible to fabricate, characterize and tailor the functional properties of the nanoparticles for their applications in different fields. With the rapid developments in fluorescence spectroscopy and microscopy, fluorescent materials have become more significant than ever for several applications such as sensors, healthcare and biomedical applications [3–8]. Also, fluorescent nanoparticles based probe have emerged as a promising platform for a variety of biological applications. For instance, Xian Jun Loh and his coworkers demonstrated luminescent upconversion material for bioimaging and biodetection techniques. They examined the recent developments in the field of luminescent upconversion material in the mechanics of TTA (Triplet–triplet annihilation) with reference to the applicability in biomedical fields [9]. A group of scientist developed efficient gene delivery platform to mouse embryonic stem cell colonies which is reported elsewhere [10]. Among different types of nanoparticles zero dimensional carbon dots (CDs), a newcomer to the globe of nanolights and nanomaterials have fascinated growing attention due to their interesting properties of sensor design, excellent biocompatibility, medical diagnosis, low toxicity, photocatalysts, tunable luminescence property, antibacterial properties and also being potential building blocks for nanodevices [11–18]. Being photoactive CDs are nonblinking and photochemically and physicochemically stable [19,20]. Due to these characteristic features they became popular in the ground of multicolor and one or two photon in bio-imaging of in vitro and in vivo [21,22]. Besides, attributing to their ample surface oxygen functionalities and hydrophilicity, CDs have been acknowledged as an auspicious

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support for construction of optical sensor for environmental pollutants and quantitative assay of biomolecules [23,24]. Their remarkable properties like robustness against photobleaching, optical absorptivity, chemical inertness, ease of functionalization, good adaptability as well as low cost augment their applicability under sundry conditions [25–30]. But, the great challenge concerning the utilization of pristine CDs is the moderate quantum yield with modest luminescence properties unveiled by intrinsic CDs. Numerous approaches including functionalization, heteroatom doping [31], surface passivation were generated to boost their photoluminescence properties and modification of CDs. Among these techniques, heteroatom doping have captured substantial attention of the scholars around the world owing to their facile nature as well as cost effectiveness [32–35]. For example, a simple hydrothermal method was reported by Yang et al. to prepare nitrogen doped CDs using citric acid and ethylenediamine with very high QY (80%) [36]. This high QY value is nearly equivalent to that of fluorescent dyes. Xu et al. reported a slimplistic way to prepare sulfur doped CDs by using sodium citrate and sodium thiosulfate [37]. Dopants like boron (B) [38], phosphorus (P) [39], silicon (Si) [33] have also been incorporated to embellish the luminescence properties of the CDs. Moreover to single heteroatom doping strategy, co-heteroatom doping approach had been also studied due to the synergistic effect between the doped heteroatoms appears to be quite beneficial. For instance, Yu et al. reported similar hydrothermal approach to synthesize sulfur and nitrogen co-doped CDs with L-cysteine and citric acid as precursors, which shows 73% QY [40].

Incorporation of metal atoms into the CDs matrix has found little advancement, comparison to the non-metal doping approach. Wu et al. reported improved electron-donating and accepting ability by co-doping the CDs with nitrogen and copper and applied them as a promising photocatalyst application [41]. Nevertheless, introduction of metal atom into CDs matrix is associated with increase toxicity. Therefore, ideal dopant metal should not provide toxicity to the CDs and also should be ecologically benign. Zinc (Zn) is a vital element assisting numerous electron transfer processes in environment. It is also a trace element for different bio-systems. It has been reported that Zn has negligible toxic character. Zn deficiency causes many health hazards. Therefore, usage of Zn as dopant into the CDs matrix is quite beneficial to enhance the properties of these zero dimensional tiny nanomaterial. In this context, incorporation of Zn has illustrated improvement of different properties, previously. Guo et al. described that the performance of photodetectors could considerably increase with the introduction of zinc oxide quantum dots/carbon nanodots hybrid films [42]. Zhang et al. reported sol-gel method to prepare ZnO/carbon quantum dot which showed an excellent photocatalytic activity [43]. Zinc doped CDs (QY 29.3%) obtained from chitosan/metal ion complex was reported by Li and his co-workers [44].

Moreover, the antibacterial activity of zinc oxide (ZnO) nanoparticles has been investigated with various non-pathogenic and pathogenic bacteria like *E. coli* and *S. aureus* [45–48]. ZnO nanoparticles are biosafe, non-toxic, biocompatible and have application in the field of drug carrier, filling in medical materials, cosmetic [49]. Previously many studies have shown the harmful effect of nanomaterials on live cells but very low concentrations of ZnO are non-toxic to eukaryotic cells [50,51]. ZnO with a wide band gap of 3.37 eV displayed a good photocatalytic activity. Various methods to prepare ZnO CDs with photocatalytic features had been reported previously. A nice overlap was found between the photoluminescence range of CDs and ZnO. Hence, there is a possibility of energy/charge transfer between CDs and ZnO due to this overlap.

Herein, we report a facile pathway to synthesized bluish white luminescence nitrogen and zinc co-doped CDs (N, Zn-CDs) with high quantum yield (QY) > 50%. These heteroatom co-doped CDs exhibits high doping efficiency comparison to other reported studies. The N, Zn-CDs were analyzed for bacteriostatic effect of gram-negative bacteria which is one of the most major foodborne pathogen in food industry. Foods of different origins, including radish sprouts, spinach, pea salad, lettuce, alfalfa, cantaloupe, raw milk, apple cider, mayonnaise, undercooked beef were associated with illnesses caused by these bacteria can give rise to critical diseases like abdominal pain with bloody stools, diarrhoea, colon inflammation etc. The as-prepared N, Zn-CDs exhibits excellent bacteriostatic effect at a very low concentration. Therefore, they can be used in plastics to prevent bacterial growth on surfaces. Moreover, N, Zn-CDs were investigated as fluorescent nano-probe for the H_2O_2 detection grounded on Fenton reaction. The facile synthesis of robust N, Zn-CDs with enhanced luminescence is anticipated to capture widespread attention and applicability.

2. Experimentals

2.1. Materials

Citric acid, tris(hydroxymethyl)aminomethane, ferrous sulfate heptahydrate, hydrogen peroxide and phosphate-buffered saline (PBS) were purchased from Sigma-Aldrich, Germany. Zinc acetate [$(Zn(O_2CCH_3)_2(H_2O)_2]$ was purchased from Merck, India. Luria-Bertani (LB) broth was purchased from Himedia, India. *Escherichia coli* (DH5α) used in this experiment were obtained from Department of Biotechnology, Indian Institute of Technology, Kharagpur. All other chemicals used were of reagent grade.

2.2. Synthesis of control CDs and Zn-doped CDs (N, Zn-CDs)

Control CDs (without Zn doping) were synthesized using simple hydrothermal method. Briefly, 25 mL citric acid solution (0.1 M) and tris(hydroxymethyl)aminomethane (0.3 M) were added into a 50 mL poly(tetrafluoroethylene) (Teflon)-lined autoclave. The temperature of the autoclave was kept fixed temperature at 200 °C for 4 h. After the reaction was over, the autoclave was naturally cooled down to room temperature. The obtained pale yellow product was centrifuged at 10000 rpm for 20 min to remove large particles and the supernatant was collected. At last, powdered sample was derived after dialysis and lyophilization. After that, Zn-doped CDs (N, Zn-CDs) was prepared using 25 mL of 0.1 M control CDs solution and 0.05 M zinc acetate. The mixture was transferred to dried poly(tetrafluoroethylene) (Teflon)-lined autoclave and kept at 200 °C for 4 h. The same process was used to carry out solid sample.

2.3. Characterization

The microstructure and morphology of the N, Zn-CDs were investigated using a high resolution transmission electron microscope HRTEM (JEOL, Japan operating voltage 200 kV with filament LaB6). The Fourier transform infrared (FTIR) spectrum of the N, Zn-CDs were recorded on a FTIR spectrophotometer (Perkin Elmer, model-Spectrum-2, Singapore) in the range of 500–4000 cm^{-1} with resolution of 4 cm^{-1} and 16 scans. Scanning electron microscopy (SEM) images of *Escherichia coli* were observed by using FESEM (Field emission Scanning Electron Microscope, MERLIN with Tungsten filament; Carl ZEISS, SMT, Germany) with the accelerating voltage set to 15 kV. The amorphous nature of the N, Zn-CDs were obtained by X-ray Diffractometer (PANalytical High Resolution XRD-I, PW 3040/60). UV–visible absorption spectrum of the prepared N, Zn-CDs in aqueous solution was performed using a UV Spectrometer (PerkinElmer, model-2 Singapore, Lambda35). Fluorescence measurements were measured on a Fluoromax_4C_1052D_4312_FM spectrofluorometer in aqueous dispersion. The fluorescence lifetime was measured at room temperature using a diode laser (Model EPL 375, Edinburg Instruments, Life Spec II) of wavelength 376.6 nm. The elemental composition and mapping of the prepared N, Zn-CDs were analyzed by energy dispersive X-ray study (EDX, INCA PentaFET ×3, Oxford Instrument UK. X-ray photoelectron spectroscopy (XPS) analysis was carried out using a commercial