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COMMUNICATION

Direct Synthesis of Highly Stable Nitrogen Rich Carbon Dots toward White Light Emission

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Here we report a single step, rapid synthetic strategy for white light emitting nitrogen rich carbon dots (NCDs) under a range of excitation wavelength by carbonizing ethylenediamine using P_2O_5 and water. The NCDs show unprecedented stability towards ultraviolet (UV) irradiation, extreme pH, and oxidative conditions, which is highly desired in light emitting diode (LED) applications.

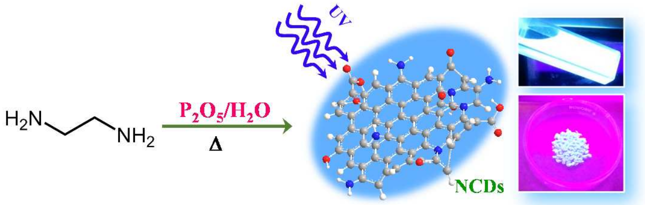
In recent times, semiconductor quantum dots (QDs) are extensively exploited in the development of white light emitting diodes (WLEDs).[1] However, need to mix blue, green and red emitting QDs restrict its use in WLEDs owing to the compatibility, cumbersome package processes as well as ease of energy transfer between QDs.[2] Also inherent toxicity and lack of stability towards harsh chemical and thermal environment further reduces its usage.[3] In an attempt to enhance the quality of phosphor material in WLEDs, researchers utilized fluorescent carbon nanoparticles (FCNPs) such as carbon dots (CDs) in its modified as well unmodified forms.[4]

Carbon dots (CDs) are carbon based benign fluorescent lanterns, which prevailed over semiconductor quantum dots (QDs) and conventional dyes in terms of stability, non-toxicity, ease of synthesis and cost.[5] Being the rising star of fluorophore family they have been employed in bioimaging,[6,7] photocatalysis,[8,9] optoelectronics,[10] and sensing.[11,12] On the other hand, FCNPs possess feeble quantum yield which hamper their practical applications.[13] Few researchers have shown that quantum yield of the FCNPs can be improved by doping nitrogen atoms.[14]

A large number of bottom up and top-down approaches being adopted to synthesize CDs and nitrogen doped CDs in recent times. However, many doping strategies demand long reaction time, high operating temperature and complex synthetic procedure, yet the amount of nitrogen incorporated is ineffective in many cases.[14, 15] Most of the synthetic strategies entail two or more precursors and utilize hydrothermal route which is time consuming and often results in lower yield.[16,17] A rapid and easy synthetic strategy for nitrogen doped CDs having high quantum yield and good stability is rare.

Furthermore, most of the FCNPs in doped and un-doped state reported so far luminesce at the blue and green portion of the visible spectrum under UV excitation and hence one need to blend with external fluorophores to achieve white phosphor material, which is undesired.[18] For example, Bin Chen and co-workers recently shown the white light emission from blue emttiing carbon dots and green, red emitting lanthanide composite films.[19] A white light emission from polymeric film containing nitrogen rich carbon dots (NCDs) with a blue emitting InGaN were also demonstrated.[20]

In this letter, we report a quick and direct strategy for synthesizing NCDs having strong resistance towards ultraviolet (UV) irradiation, pH and oxidative environment. The synthesis was achieved using a single precursor molecule, ethylenediamine. Interestingly, the NCDs exhibited white light emission under 365 nm UV light source, an unusual feature. A nearly white light emission from carbon based fluorescent nanomaterial, which is obtained from facile synthetic route using a single precursor without compromising the stability is the captivating features of the present report.



Scheme 1 Synthesis of NCDs by carbonization of ethylenediamine. Photographs (solution phase (top) and solid powder (bottom)) show white light emission under 365 nm UV light.

The NCDs were prepared by carbonizing ethylenediamine (EDA) using P_2O_5/H_2O as carbonizing agent according to Scheme 1.

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Detailed synthesis procedure is given in experimental section, ESI. EDA can act as nitrogeneous carbon source. The heat produced due to the exothermic reaction between P_2O_5 and H_2O carbonizes the EDA precursor. Here the upper temperature of the reaction was controlled by the vaporization of EDA (boiling point of EDA is 116 ^{0}C), as the vaporization removes excess of heat produced during reaction. Hence, vaporization of EDA also serves to restrict the size of the nanoparticles by limiting the reaction temperature. Polyphosphoric acid produced during the intermediate stage catalyzes the reaction and traps the EDA vapors.[7] The crude carbonized product was diluted and centrifuged several times and the supernatant was dialysed before used for further studies. Quantum yield of purified NCDs measured using quinine sulphate as standard ($\phi_{ref} = 0.54$) (see ESI for quantum yield calculations) at 360 nm excitation was 28.5%, which is superior to many of the doped and un-doped CDs.[10,11,13,16]

Transmission electron microscopy (TEM) images (Fig. 1A) of NCDs show near spherical morphology with size of the dots range from 2 to 5 nm as shown by the histogram (inset Fig. 1A). Atomic force microscopy (AFM) images of NCDs also support the formation of quasi spherical dots with an average height $\leq$3 nm, indicating the thickness equivalent to $\leq$5 graphene layers. AFM image of NCDs and corresponding histogram (in terms of height) has shown in Fig. S1, ESI.

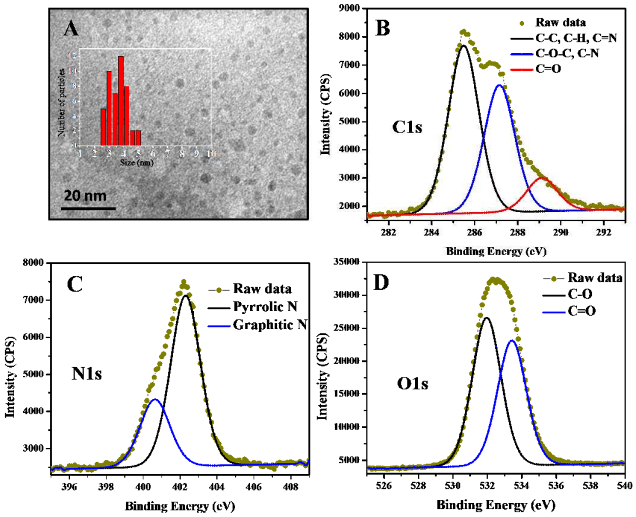

Fig. 1 (A) TEM image of prepared NCDs, inset: Histogram showing the size distribution. (B), (C) and (D) are the high resolution XPS spectra of C1s, N1s and O1s, respectively.

Detailed spectroscopic analysis has been carried out to explore bonding and elemental composition in NCDs. Survey scan X-ray photoelectron spectrum (XPS) of NCDs displayed P2p, C1s, N1s and O1s peaks, at 134.5, 286.0, 401.8 and 532.3 eV, respectively (Fig. S2, ESI). The C1s peak at 286.0 can be deconvoluted into three peaks centered at 285.5, 287.2 and 289.1 eV which are ascribed to C-C/C-H/C-N, C-O-C/C=N and C=O bonds, respectively (Fig. 1B).[15,21] High resolution N1s spectrum (Fig. 1C) shows the presence pyrrolic/N-H (400.6 eV) and graphitic (402.3 eV) nitrogen which verifies the incorporation of nitrogen atoms into NCDs.[15,22] Similarly, the deconvoluted O1s spectrum (Fig. 1D) depicts the presence of C-O (532.0 eV) and C=O (533.4 eV) bonds.[20,21] A low intensity peak observed at 25 eV is attributed to O2s.[23] High oxygen content shown by the XPS spectrum of NCDs compared to carbon and nitrogen atoms are mainly due to the adsorbed H_3PO_4 and H_2O molecules. Peak at 134.5 eV and 191.6 eV is assigned to P atom of phosphoric acid. High resolution P2p spectrum (Fig. S3, ESI) shows only one peak centered at 134.5, which corresponds to P-O/P=O bond of H_3PO_4.[24] This ruled out the possibility of incorporation of P atoms into NCDs.

Fourier Transform Infrared (FTIR) spectrum (Fig. S4, ESI) reveals the formation of NCDs with N and O containing functional groups. The peaks at 1562/1511 and 3020 cm^{-1} due to C=C (aromatic) and C-H (aromatic), respectively suggests the formation of carbon containing ring structure. 1638 and 1744 cm^{-1} bands are assigned to the stretching vibrations of C=N and C=O bonds, respectively.[4,14] Broad vibrations at 3430 cm^{-1} is indicating the presence of N-H (aromatic)/O-H groups.[4,16] Bands at 1070, 1090, and 1259 cm^{-1} suggest the presence of C-O/C-N containing functional groups.[4,20,16] These functional groups affirmed the excellent water solubility to NCDs. Compared to EDA, N-H bending vibration at 1595 cm^{-1} and aliphatic N-H stretching at 3278 cm^{-1} are significantly weakened in the case of NCDs, which reflects the successful carbonization of ethylenediamine.[20] Raman spectrum showed a strong D band at 1332 cm^{-1} and a weak G band centred at 1557 cm^{-1} (Fig. S5, ESI). Weak G band is the direct result of incorporation of large number of N atoms into the graphitic core.

UV-Visible absorption spectra further support incorporation of hetero atoms into the carbon core (Fig. S6, ESI). For NCDs, four characteristic electronic transitions around 230, 275, 335 and 385 nm were observed. The peaks at 230 and 335 nm are respectively assigned to π–π^* absorption from aromatic sp^2 domains and n–π^* absorption of C=O group. The latter peak is strongly red shifted compared to the reported N-free CDs.[15] The absorption at 275 nm may be due to the C=N group, similar observation is made by Tang et al.[15] Low energy absorption feature at 385 nm is possibly through J-type aggregation as reported by Tufan et al.[25,26]

The above microscopic and spectroscopic analysis confirms the successful synthesis of NCDs with a size around 2-5 nm and having abundant nitrogen atoms present in core (as graphitic N and pyrrolic N) as well as at the surface (as -NH_2) along with oxygen containing functional groups (carboxyl and hydroxyl).

The emission spectra of NCDs at various excitation wavelength follows typical excitation dependent emission (Fig. 2A) which is a commonly observed phenomenon in FCNPs.[15] As shown in Fig. 2A, fluorescence spectra of NCDs collected at various excitation wavelength spans large portion of the visible region of electromagnetic spectrum including blue, green, and red region, rationalizing white light emitting behaviour. Under 365 nm UV source the NCDs show white light emission (Fig. 2C). The CIE (Commission Internationale d'E´ clairage) 1931 chromaticity coordinates calculated using steady state emission spectra corresponds to the excitation wavelengths of 300, 320, 340, 360, 380 and 400 nm are found to be (0.26,0.41), (0.25,0.39), (0.24,0.38), (0.22,0.33), (0.21,0.32), (0.22,0.33), respectively. These CIE coordinates are located within the breadth of white light in the chromaticity diagram shown in Fig. 2B. But, due to the lack of red emission intensity compared to blue and green emission from NCDs, the CIE coordinates are away from pure white light emission coordinates (0.33, 0.33). Effort to enhance purity of white light emission from NCDs is under progress. It should be noted that solvent dependent fluorescence studies were not performed due to the lack solubility of NCDs in organic solvents.

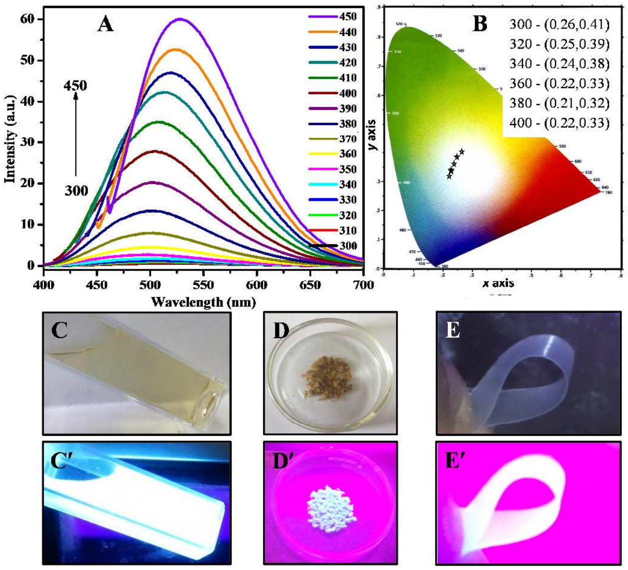

Fig. 2 (A) Photoluminescence spectra of NCDs at various excitation wavelengths. (B) CIE chromaticity diagram showing the chromaticity coordinates at excitation wavelengths 300, 320, 340, 360, 380 and 400 nm. (C), (D) and (E) are the visible light photographs of NCD solution, NCD solid powder and NCDs coated over a polymeric surface, respectively. C′, D′ and E′ are the corresponding photographs under 365 nm UV light showing white light emission.

Photoluminescence excitation (PLE) spectra of NCDs at various emission wavelengths; 410 to 680 nm (Fig. S7, ESI) have been measured. In general, PLE spectrum shows two peaks, a shoulder band around 370 nm (3.35 eV) and a longer wavelength band at 405-480 nm (3.06-2.58 eV). The latter is red shifted when the emission wavelength is increased whereas former remains unchanged. Similar observation has been reported for N-doped CDs.[15]

Detailed fluorescence lifetime measurements were done to investigate the broad emission from NCDs under 330 nm excitation. Excited state luminescence decay profile collected at 400, 450 and 500 nm (Fig. S8, ESI), exhibits bi-exponential fit in all the cases. The average lifetime, corresponding relative amplitude and CHSQ2 values are shown in Table S1 of ESI. Here the shorter lifetime component may be imputed to the direct recombination process whereas longer one must have aroused from trap/edge states.[15,27] It is clear from the Table S1 that longer lifetime component (τ_2) as well its corresponding amplitude is increased but the shorter lifetime component (τ_1) remains unchanged as the collection wavelength is increased. This in turn led to the increase in average lifetime of NCDs from 5.21 to 6.59 ns when emission wavelength is increased from 400 to 500 nm. Therefore it is clear that these emissions are from different states. Hence the presence of large number of emissive states produced by C=C/C=N core as well as various oxygen and nitrogen containing functional groups at the surface explains the observed broad steady state fluorescence spectra of NCDs responsible for white light emission. Broad emission may be originated from the direct recombination of exciton as well as emission from the intermediate energy levels resulted from nitrogen and oxygen containing functional groups. Based on the above observations a plausible emission states has been proposed in Fig. S9 of ESI.[15] It is clear from the figure that absorption of light radiation of certain energy pumps π electrons of sp^2 hybridized carbon (C=C, C=O and C=N) to the corresponding π^* antibonding orbitals. Now the electrons present in higher energy level can decay in two ways, one via direct recombination process and other by intersystem crossing followed by radiative recombination. Hence the presence of large number of emissive states explains the nearly white light emission as a consequence of broad emission band from NCDs.

For solid-state device applications, fluorophore's luminescence should be retained when fabricated onto solid surface without compromising its stability. A large number of organic molecules and semiconductor quantum dots which fluoresce strongly in solution fail to emit when coated over the solid surface due to the aggregation induced quenching.[28,29,30] Steady state emission spectra shown in Fig. S10 of ESI depict the emission profile of NCDs coated over the polyvinyl alcohol (PVA) films (see the photograph given in Figure 2E). Emission spectra measured at various excitation wavelength are similar to the one shown in the solution state. Hence, the ability to retain its luminescence when coated over the polymeric surface makes NCDs a highly attractive candidate for solid state device applications.

The NCDs showed excellent stability in various optical and chemical environments. Photoluminescence spectra of NCDs under various pH were recorded (Fig. 3A) and Fig. 3B shows a plot of photoluminescence intensity against pH. Unlike CDs and semiconductor QDs, NCDs were highly stable at extreme pH conditions. This may be due to the presence of large number of nitrogen containing functional groups such as amide, amine, nitrile etc. which are less prone to aggregation compared to carboxyl and hydroxyl functional groups as in CDs. The tendency of aggregation in CDs is found to increase with pH of the medium.[25,26] In the case of CDs, with the increase of pH, conversion of –COOH rich CDs to –OH rich CDs occur due to the deprotonation of –COOH. Subsequently a strong intermolecular hydrogen bonding between carboxylate and hydroxyl groups is expected. But, in the present case a significant number of nitrogen containing functional groups are available for NCDs. This must have reduced the extent of aggregation when the pH of NCDs solution is changed from pH 2 to pH 10. It is clear from the UV-visible absorption spectrum that the peak at 385 nm, which is due to the formation of aggregates[25] is slightly decreased at pH 10 (Figure S11, ESI). Also, compared to the solution at pH 2, the peaks at 335 nm (due to carbonyl group) and 275 nm (due to nitrogen containing functional groups) are blue shifted at pH 10. At higher pH, the protonated form of C=N group convert to deprotonated form, thereby strengthening of π bond and hence an increase in π–π* absorption. This will result a blue shift in 275 nm absorption. The change of chemical environment of nitrogen containing functional groups might have influenced the electronic transitions of C=O, which led to the blue shift in 335 nm absorption. Such influence of nitrogen containing functional groups on the C=O energy levels are reported in the literature.[15,31]

To verify the stability in the oxidative environment, NCDs were subjected to react with concentrated HNO_3 and there was no appreciable change in the photoluminescence intensity (Fig. S12, ESI).

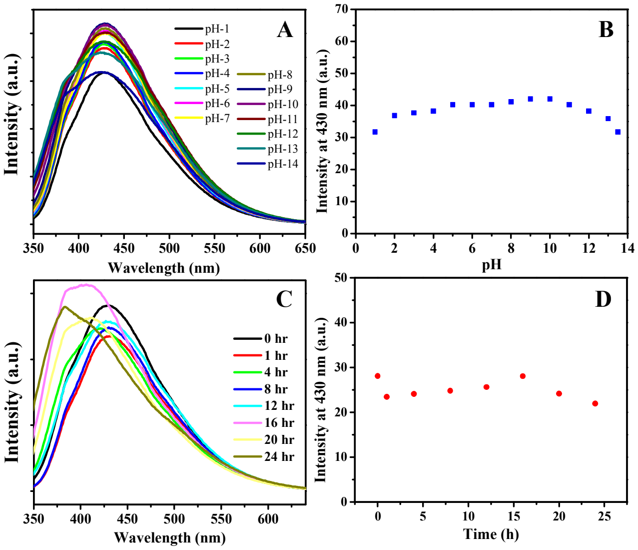

Fig. 3 (A) Photoluminescence spectra of as prepared NCDs at different pH conditions, inset: PL intensity at 430 nm at different pH. (B) Photoluminescence spectra of NCDs irradiated at different time intervals (lamp power: 48 W, wavelength of the light: 365 nm), inset: PL intensity at 430 nm at different time interval.

Further, optical stability of the NCDs were tested by illuminating with 48 W power 360 nm UV light source. Emission intensity of NCDs was unchanged with continuous irradiation for 16 h, which is superior to the many carbon and semiconductor based QD fluorescent nanoparticles (Fig. 3C), [16] change in the emission spectra after 16 h of irradiation can be attributed to the conversion/ decomposition of few labile surface functional groups such as COOH, which lead to the blue shift in the emission spectrum of NCDs (Fig. 3C). Additionally, thermogravimetric analysis (TGA) reveals that NCDs are stable up to 600°C (Fig. S13, ESI). These observations demonstrate the excellent stability of NCDs, which is a pre-requirement for fabrication of WLED devices.

In conclusion, we demonstrated an easy and a rapid strategy for synthesizing NCDs under mild condition by carbonizing ethylenediamine using P_2O_5 in the presence of water. Reaction was accomplished within two minutes. An interesting property of the present material is its nearly white light emission behaviour. Presence of large number of emissive states explains the broad emission band. In addition, NCDs manifested an unprecedented stability towards UV light, pH and oxidative environments. Hence, this class of material is a promising alternative to semiconductor QDs and organic dyes in optoelectronic applications.

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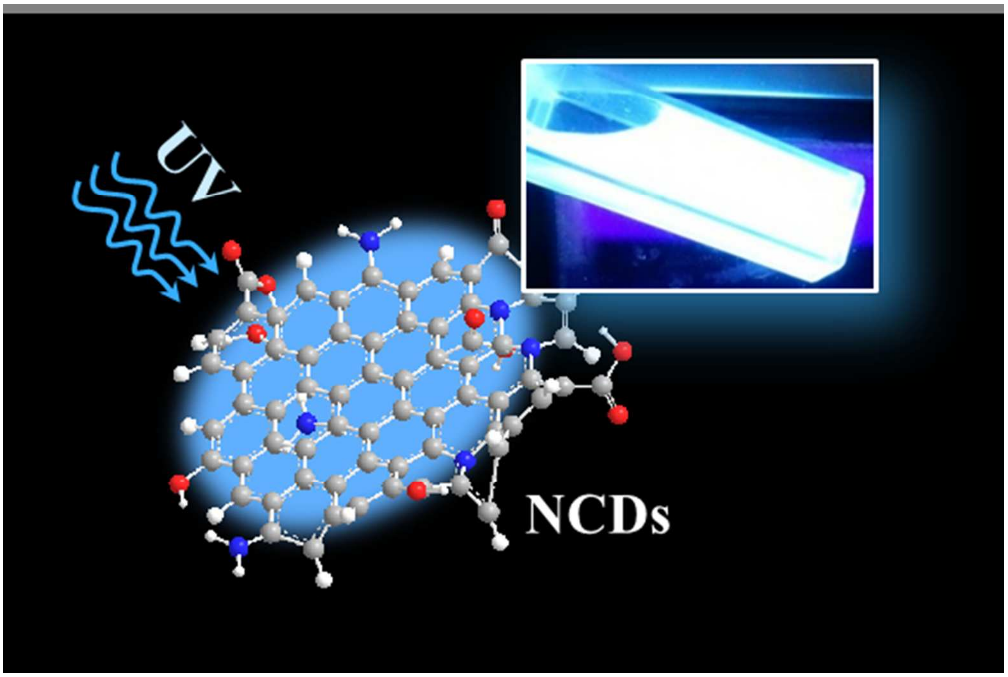
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NCDs