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## COMMUNICATION

## Fast one-step synthesis of N-doped carbon dots by pyrolyzing ethanolamine

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**The nitrogen-doped carbon dots (N-CDs) with high yield were directly synthesized by pyrolyzing ethanolamine under air environment within 7 minutes. The obtained N-CDs possess bright blue luminescence, excitation- and pH-dependent luminescence. This one-step strategy would enable a viable route towards the commercial synthesis of the N-CDs.**

In recent years, the fluorescent carbon dots (CDs) have been receiving increasing attention due to their tunable surface functionalities, outstanding optical properties, chemical stability, biocompatibility, and low toxicity,<sup>1-4</sup> which have been widely used as photonics, biotech, chemical and biological sensing, and solar energy. In the past several years, tremendous efforts have been made to develop synthetic methods for the CDs, which can be classified into two main groups: top-down and bottom-up methods.<sup>5-13</sup> For the top-down method, it suffers from some disadvantages, such as the requirement of special equipment, low yield, the damage on the aromatic carbon framework, and the non-selective “top-down” chemical cutting process, which does not allow precise control over the morphology and the size distribution of the products.<sup>11, 14</sup> Conversely, the “bottom-up” methods offer us exciting opportunities to control the CDs with well-defined molecular size, shape, and thus properties.<sup>15</sup> There have been some reports on the direct synthesis of fluorescent carbon nanoparticles from readily available natural bio resources, such as orange juice,<sup>16</sup> chicken eggs.<sup>17</sup> Some organic precursors, such as glucose and citric acid, have also shown great potential for the preparation of CDs via pyrolysis or carbonization under carbonization under certain conditions, such as hydrothermal and microwave-assisted method.<sup>10, 18-20</sup> Nevertheless, these “bottom-up” methods always involve complex synthetic procedures, time-consumption, a large amount of acid or alkali, rigorous experimental, low production yield and the special organic precursors those may be difficult to obtain. Currently, only the microwave-assisted method can be used to synthesize the CDs in a short time.<sup>5, 10, 21-23</sup> However, it always needs water as solvent and couldn't synthesize CDs in large-scale. Giannelis *et al.*<sup>3</sup> obtained strongly photoluminescent nitrogen (N)-doped CDs (N-CDs) by the pyrolysis of citric acid and ethanolamine at 230 °C for one hour. Dong *et al.*<sup>24</sup> prepared blue

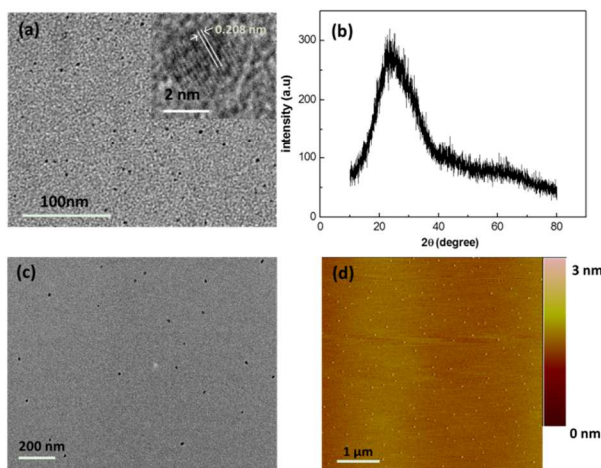
luminescent graphene quantum dots (GQDs) by directly pyrolyzing citric acid and post-treatment with NaOH solution. So the fabrication of CDs via pyrolyzing organic precursors under air environment was always low product yield or complex purification process. It is more suitable for industrial-scale production if one can pyrolyze one kind of matter under air environment in a short time.

In this communication, we reported a novel and large-scale-strategy for the synthesis of the N-CDs with high yield by pyrolyzing low-cost ethanolamine under air environment within just 7 minutes. During the synthesis procedure of the N-CDs, ethanolamine serves as both carbon source and nitrogen source, and the hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) was demonstrated to improve the pyrolysis process. To the best of our knowledge, this is the first time to synthesize the N-CDs just via pyrolyzing ethanolamine under air environment in a short time. The synthesis strategy of the N-CDs is very simple and doesn't need any solvent, acid or alkali, complex equipment, which is economical and suitable for industrial-scale production.

The N-CDs were synthesized by pyrolyzing ethanolamine under air environment (see Supporting Information for experimental details). In a typical procedure, the ethanolamine (3 ml) in a beaker (100 ml) was pyrolyzed in the stove at 150 °C under air environment. After 2 hour, the N-CDs were obtained, references as N-CD1. To shorten the reaction time and increase the production yield, the mixture of ethanolamine (3 ml) and H<sub>2</sub>O<sub>2</sub> (4.5 ml) was put into the stove at 250 °C and kept for 7 minutes to obtain N-CDs. The as-prepared N-CDs were marked as N-CD2.

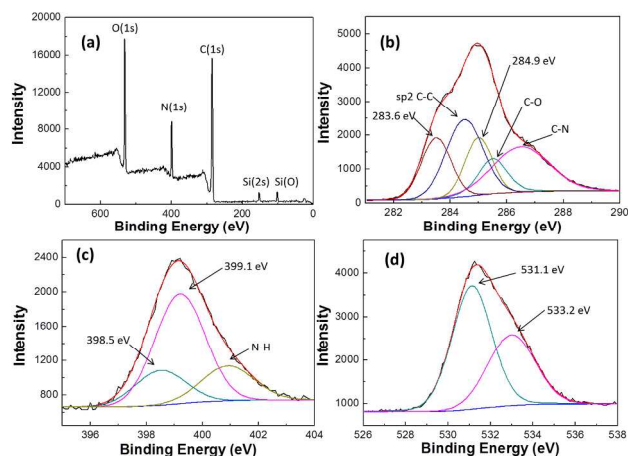
The as-prepared NCDs own high solubility in aqueous and a wide range of organic solvents (such as dimethyl formamide, ethanol), confirming the high content of surface polar organic groups. Typical transmission electron microscopy (TEM) images are shown in **Fig. 1a**, it can be seen that the as-prepared N-CD1 have uniform dispersion without apparent aggregation and a mean particle diameter of 2.7 nm. Well-resolved lattice fringes with an interplanar spacing of 0.208 nm can be observed clearly (**Fig. 1a** insert), which is close to the (100) facet of graphite.<sup>25</sup> The X-ray diffraction (XRD) pattern of the N-CD1 in **Fig. 1b** shows a broader (002) peak centered at around 23.5°, corresponding to the interlayer spacing *d* of 0.38 nm which is larger than in graphite (0.34 nm). The increase in *d* value indicates that an increase in amorphous nature is attributed to the introduction of more oxygen containing groups.<sup>9</sup> From TEM images

in **Fig.1c**, the as-prepared N-CD2 have uniform dispersion without apparent aggregation and a mean particle diameter of 8.3 nm. A typical atomic force microscopy (AFM) image (**Fig.1d**) shows that



**Fig. 1** (a) TEM and HRTEM images (inset) of the as-prepared N-CD1, (b) XRD pattern of the as-prepared N-CD1, (c) TEM images and (d) AFM image of the prepared N-CD2.

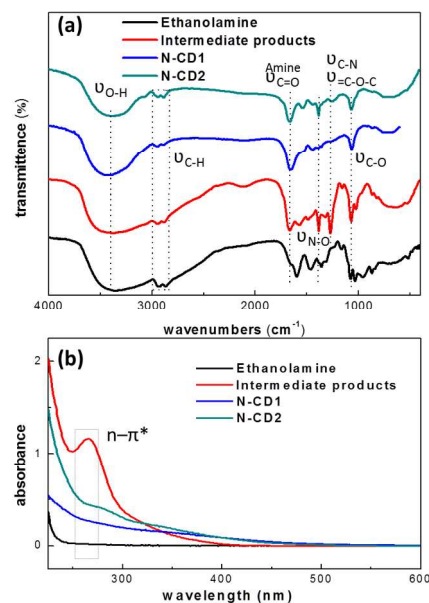
the topographic height of the as-prepared N-CD2 is mostly distributed in the range from 1.0 to 2.5 nm, with an average value of 2.0 nm. The Raman spectra of both the N-CD1 and the N-CD2 (**Fig.S3**) display two broad peaks at around 1365 and 1575  $\text{cm}^{-1}$ , which are attributed to the D band ( $sp^3$ -hybridized) and G band ( $sp^2$ -hybridized), respectively.



**Fig. 2** (a) XPS spectra of the N-CD1. (b)–(d) High-resolution  $C_{1s}$ (b),  $N_{1s}$ (c), and  $O_{1s}$ (d) peaks of the N-CD1.

To further characterize the as-prepared N-CDs, X-ray photoelectron spectroscopy (XPS) was used to investigate the surface groups of the N-CD1. As shown in **Fig.2a**, the results show that the N-CD1 are mainly composed of carbon, nitrogen, and oxygen. The high-resolution spectra of  $C_{1s}$  (**Fig. 2b**) exhibits five main peaks. The binding energy peak at 284.5 eV confirms the graphitic structure ( $sp^2C$ - $sp^2C$ ) of the N-CDs. The binding energy peaks at 283.6 and 284.9 eV are mainly vacancy defects, pentagon-heptagon, and  $sp^2C$ - $sp^2C$  influenced by functional groups. The peaks

at 285.5 and 286.5 eV suggest the presence of C-O and C-N. The high-resolution spectra of  $N_{1s}$  (**Fig. 2c**) reveal the presence of pyridinic type (398.5 and 399.1eV), the binding energy of 400.9 eV is associated with N-H groups.<sup>26</sup> The high-resolution spectra of  $O_{1s}$  (**Fig. 2d**) reveal the presence of C=O-containing groups (531.1 eV)<sup>27, 28</sup>, the binding energy of 533.2 eV is associated with  $sp^2C$ -OH and cyclic ether-containing groups (C-O-C, C=C-O-C). From the quantitative determination by XPS (**Table S2**), 13.84 % of nitrogen and 68.11% of carbon indicate that the as-prepared CDs are the nitrogen-doped and carbon-rich, indicating the sufficient carbonization.



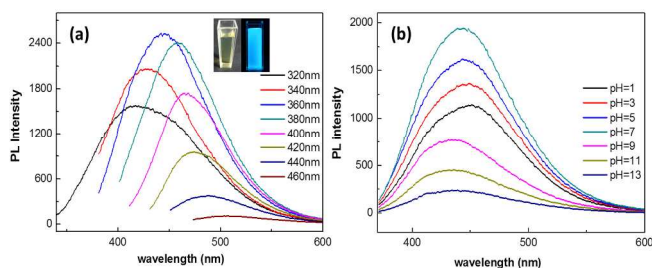
**Fig. 3** (a) Typical FTIR spectra and (b) UV-vis absorption of ethanolamine, intermediate products, N-CD1 and N-CD2.

Under the experimental process used in this study, the ethanolamine was oxidized firstly, then the color of liquid changed from colorless to bright yellow liquid meaning “polymerization” step in progress and then dark at last meaning “carbonization” steps finishing. The “polymerization” step and “carbonization” steps are similar to other reports<sup>3, 7, 18</sup>. In order to study the process, FTIR (**Fig. 3a**) and UV-vis absorption (**Fig. 3b**) were used to characterize ethanolamine, intermediate products (bright yellow liquid after “polymerization” step), the obtained N-CD1 and N-CD2. As shown in the FTIR spectra (**Fig. 3a**), these are some emerging peaks of intermediate products. The peak at 1360  $\text{cm}^{-1}$  confirms the symmetric stretch of N-O, this is due to oxidized amido. The peak at 1668  $\text{cm}^{-1}$  of the intermediate products declares that the C=O stretching of the amide bond and vibrational fingerprints centered at 1570  $\text{cm}^{-1}$  (N-H in-plane bending) confirms the presence of amide functional groups. The peak at 1271  $\text{cm}^{-1}$  declares stretching vibration absorption peak of Benzene ring linked tertiary amine or aryl ethers (=C-O-C) band, the peak at 1068  $\text{cm}^{-1}$  declares symmetrical stretching vibration absorption peak of aryl ethers (=C-O-C) band. Those new bonds indicate extensive cross-linking reactions between ethanolamine or its oxidative products, indicating the “polymerization” is in progress. When the yellow liquid turned to black gel, the “carbonization” process finished. In the FTIR spectra (**Fig. 3a**) of N-CD1 and N-CD2, the peak at 1271  $\text{cm}^{-1}$  and 1360  $\text{cm}^{-1}$  become less or even disappeared, indicating that most of tertiary amines or nitro groups are consumed for the buildup of the



carbogenic core. From the UV-vis spectra, one can see that the intermediate products also exhibit peaks at 280 nm, which are ascribed to the typical absorption of the  $n-\pi^*$  transition of C=O or N=O in  $sp^3$  hybrid regions.<sup>29</sup> So in the "polymerization" step, many C=O or N=O bonds appeared. When the "carbonization" step finished, the 280 nm peaks become weaker or even disappeared, this is due to that the nitro groups are consumed. This experimental evidence unambiguously suggests that amide functional and nitro groups may play a key role in the process from "polymerization" to "carbonization". The formation of imide derivatives during pyrolysis has been reported in previous literature.<sup>30</sup> Therefore, we deduced that buildup of carbogenic core is attributed to further cross-linking reactions of the intermediate products with amide functional or nitro groups groups. The oxidation of amines and the "polymerization" and "carbonization" steps, however, are all very complicated, the formation mechanism of the CDs requires further investigation in the future work.

In the synthesis process of N-CD1, as the oxidation of ethanolamine only occurred in the air-liquid interface, the oxidation and "polymerization" step was very slow and needed ca. 1 hour, amounts of ethanolamine were volatilized and the product yield was just 6 % (Table S1). In the synthesis process of N-CD2, the  $H_2O_2$  was miscible with ethanolamine and accelerated the oxidation process of ethanolamine, at the same time the higher temperature can accelerate the "polymerization" and "carbonization" step. So the time of whole synthesis process of N-CDs is shortened from 2 hours to just several minutes. The intermediate products after the "polymerization" is very hard to be volatilized, so much smaller amount of ethanolamine are volatilized and one could get higher product yield (Table S1). The reaction temperature is also important for N-CD2 carbonization, the rules determined for temperature effects on N-CD2 was also studied (Table S1). There is nearly no fluorescence of intermediate products (Fig. S2), indicating that intermediate products don't contain organic fluorophores. This is different from the report on pyrolysis of citric acid and ethanolamine.<sup>3</sup>



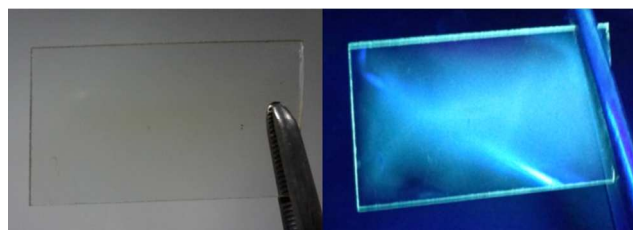
**Fig. 4** (a) Excitation and emission spectra for the as-prepared N-CD2 dispersed in water at excitation wavelengths progressively increasing from 320 to 460 nm. Inset are photos of aqueous solution under room light (left) and 365 nm irradiation (right). (b) PL spectra of the N-CD2 at 360 nm excitation for different pH values.

To study the optical properties of the N-CDs, the detailed photoluminescence (PL) measurements of the N-CD1 (Fig. S4) and N-CD2 (Fig. 4a) were carried out by using different excitation wavelengths. The luminescence spectra of N-CD2 in water show a maximum at 445 nm with the strongest intensity recorded for  $\lambda_{ex}$  = 360 nm. The emission peak shifts from ca. 400 to ca. 500 nm while excitation wavelength changes from 320 to 460 nm, which is similar with the most CDs in the previous literatures.<sup>7,18,21</sup> The N-CD1 also shows the same property (Figure S4). Excitation-dependent PL behavior was observed, which is common in fluorescent carbon materials<sup>7,18,21</sup>. This behavior is contributed to the surface state affecting the band gap of CDs.<sup>1</sup> The surface state is analogous to a

molecular state whereas the size effect is a result of quantum dimensions, both of which contribute to the complexity of the excited states of N-CDs. Bright blue luminescence under the illumination of UV light (365 nm) of the N-CD2 aqueous solution can be seen clearly (Fig. 4a inset).

The fluorescence quantum yield (Fig. S5) of the as-prepared N-CDs excited with 360 nm UV light was improved from 7 % to 10.3 % after adding  $H_2O_2$ , using quinine sulfate (54.6 % in 0.1M sulfuric acid) as a reference, which maybe on account of the more surface passivation agents through  $H_2O_2$  treatment. The fluorescence lifetime ( $\tau$ ) of N-CDs was assessed by time-resolved photoluminescence measurements. The fluorescence lifetime of both N-CD1 and N-CD2 was calculated to be 4.6 ns according to the fluorescence decay profile with excitation wavelengths in 360 nm and emission wavelengths in 450 nm (Fig. S6). It represents that the fluorescence decay profile of N-CDs with single exponential decay kinetics. The short lifetime of N-CDs is indicative of the radiative recombination of the excitons.<sup>5,6</sup> The N-CDs are very stable in the solution. Even after being kept for 6 months in air at room temperature, it still exhibits a transparent appearance and strong PL emission. This stability is attributed to the structural integrity and crystallinity of the N-CDs.

The pH dependent PL behavior of the N-CD2 was also investigated, as shown in Fig. 4b. The pH value was adjusted by adding NaOH or  $H_2SO_4$ . The PL intensity decreased very obviously at high pH value and slightly decreased at low pH value. So the PL intensity was more sensitive to basic conditions than under acidic conditions, PL emission wavelength a little blue shift at basic conditions and red shift at acidic conditions. This phenomenon is due to the surface state strongly affected by the pH of solvent. The optical pH-sensitive of the N-CDs could be exploited for pH sensor for pH measurement.



**Fig. 5** The carbon dots fluorescent film under room light (left) and under 365 nm irradiation (right).

Highly-dense immobilization of carbon dots into flexible organic thin films is an indispensable procedure for their wide applications, so we extended the use of N-CDs as carbon dot fluorescent film. The N-CD2 was blended into a compatible PVA solution to form thin films by coating the glass and drying at 70 °C. Fig. 5 shows photographs of the glass with carbon dots fluorescent film under room light (left) and under 365 nm irradiation (right). It could be seen that the carbon dots fluorescent film owns certain transparency under visible light and blue fluorescent under the 365 nm irradiation.

## Conclusions

In summary, we have proposed a simple and efficient one-step strategy for the fabrication of N-CDs by pyrolyzing ethanolamine under air environment within 7 minutes.  $H_2O_2$  was added to assist the pyrolysis process. The as-prepared N-CDs possess excellent stability, excitation- and pH-dependent PL behavior. We have also extended the use of N-CDs as carbon dot fluorescent film. Significantly, our strategy to prepare N-CDs is ready scalability,

high yield, economical and suitable for industrial-scale production.

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## Notes and references

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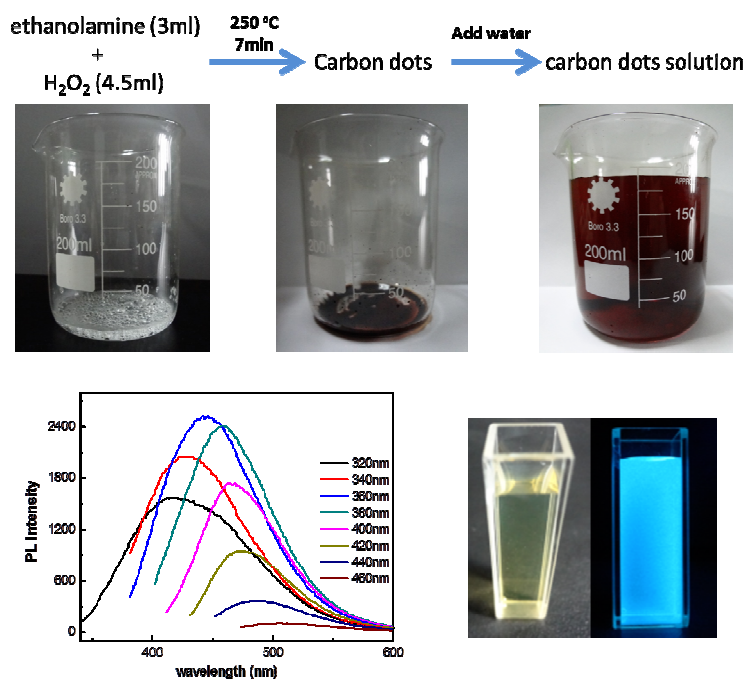
† Electronic Supplementary Information (ESI) available: Detailed experimental process, Characterization, Raman spectra and fluorescence decay, the influence of reaction temperature of the as-synthesized N-CDs. See DOI: 10.1039/b000000x/

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## Graphical Abstract

## Fast one-step synthesis of N-doped carbon dots by pyrolyzing ethanolamine

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The N doped CDs can be obtained directly with high yield by pyrolyzing ethanolamine under air environment within just 7 minutes with the assist of hydrogen peroxide.