Facile Synthesis the Nitrogen and Sulfur Co-doped Carbon Dots for Selective Fluorescence Detection of Heavy Metal Ions

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Abstract

In this article, we prepare the nitrogen (N) and sulphur (S) co-doped carbon dots (NS-CDs) via a one-step hydrothermal method using the methionine as the precursor. The N and S doping content reach as high as 15.2 *at.%* and 19.5 *at.%*, separately. The analysis of the photoluminescence dates exhibits that the relationship between the excitation and the corresponding emission wavelength can be summarized as a linear fitting function. In addition, the as prepared NS-CDs also exhibits sensitive detection properties for heavy metal cations. With these excellent characteristics, there are extensive potential applications for NS-CDs in industry and environmental monitoring.

Keywords

Co-doped carbon dots; Carbon materials; Luminescence; Heavy metal ion-detection.

1 Introduction

The carbon dots (CDs) has attracted considerable attention because of their excellent chemical, optical, mechanical and electronic properties. Carbon dots are zero dimensional (0D) quasi-spherical carbon nanoparticles with diameters less than 10 nm^{1,2}. Nitrogen and sulfur atoms have the comparable atomic size (the radius of C: 0.77 Å, N: 0.75 Å), strong valence bonds and similar electronegativity (electronegativity of C:2.55, S:2.58) with carbon atoms, they are both considered to be the excellent chemical atoms to improve the property of the carbon dots. Herein, we report an effective method to prepare **NS-CDs** in an autoclave using methionine as the precursor. The methionine is chosen for its abundance and cheapness and it is also the original sources of both N and S atoms. N and S atoms can be doped into the product at the same time and the other sources of N and S (such as ammonia and powdered S) are not needed any more which effectively avoids the soak of the other impurities. All these advantages make the methionine suitable to produce plentiful carbon dots with excellent properties in industry which exhibits potential applications in the future.

2 Experimental

The **NS-CDs** are synthesized in a typical pyrolysis process, 0.35g methionine is added into 30 ml ultra-pure water. After stirring drastically for several minutes, the mixture becomes a homogeneous solution and is transferred into a teflon-lined autoclave. **Then the slightly green NS-CDs sample is obtained at 180°C for 6 hours in an autoclave.** In the followed

steps, different concentration of metal salts solutions are prepared separately. When different metal ions are added into the carbon dots, by analyzing these characterization results, special ion is distinguished from the others. All samples are investigated by transmission electron microscopy (TEM), X-ray photoelectron spectra (XPS, PHI-5702, Physical Electronics), Fourier transform infra-red spectra (FTIR) and Raman respectively.

3 Results and discussion

As it is exhibited in the Fig.1a, the as prepared NS-CDs are well poly-dispersed and the mean diameter is 2.1 nm. Size distribution (Fig. 1b) analysis shows that the diameter of the carbon dots mainly distributes in the range of 1.2-2.8 nm. Although it is the poly-disperse that an inevitable problem when the teflon-lined autoclave is cooled to room temperature gradually and slowly, more than 72% of the products are included in a narrow range. Compared with the previously reported results, the radius of the carbon dots obtained by the methionine is similar to that reported N-CDs (3.15nm)³ prepared by the solvo-thermal process and smaller than that synthesized by the ultrasonic reaction (6.5nm)⁴. It is usually unavoidable that some dots would connect with each other to form the larger-sized NS-CDs.

Figure 1. (a) TEM image of NS-CDs. (b) Size distribution and histogram of the NS-CDs.

The figure of XPS provides the composition of elements and their chemical states. As shown in the Fig. 2a, the XPS full-spectra exhibits the C 1s peak at ca.284.3 eV, the N 1s peak at ca.401 eV, the O 1s peak at ca.531.3 eV, the S 2p peak at ca.163.9 eV and the S 2s peak at ca.229.1 eV, respectively. It is also calculated that the content of the N and S reach as high as 15.2 at.% and 19.5 at.%, which indicates that both of the N and S have been doped into the NS-CDs successfully. As shown in the fine C spectrum (Fig. 2b), distinct peaks at 284.5 eV, 285.2 eV, 286 eV and 288.1 eV are attributed to the C-C, C=N and C-S (overlapped with each other), C-N (C=O) and COOH^{5,6}, respectively. The high resolution spectrum of S 2s (Fig. 2d) can be fitted into two peaks at 163.2 eV and 164.3 eV, which would correspond to the -C-S-C- 2p 2/3 and -C-S-C- 2p 1/2 bonds respectively⁷⁻⁹. The high resolution spectrum of N 1s peak (Fig. 2c) reveals that the nitrogen mainly exists in the form of pyrrolic-N and partial lactam and imide N (~ 400.3 eV), there are also some N-H (~ 401.1 eV) groups within the resultant carbonaceous structure⁶. What is more, the possible synthesis mechanism has been shown in the Scheme S1. There is a preliminary amidation of methionine and the precursor is carbonized and pyrolyzed to form NS-CDs under the hydrothermal condition. The FT-IR spectrum in Fig. S1 further reveals that the peaks at 1010~1106 cm⁻¹ and 1210 cm⁻¹ are assigned to the stretching vibrations of C-O-C and C-OH, respectively, which make the NS-CDs exhibit a high solubility in the hydrophilic solvents without further chemical modifications. The state of S is further confirmed based on the featured peaks of 670 cm⁻¹ (stretching vibrations of C-S)^{10,11}. Beyond that, the broad peak at 3434 cm⁻¹ corresponds to the carboxylic acid and hydroxyl groups and the peak of 1570 cm⁻¹ to 1720 cm⁻¹ is attributed to the vibrations of C=C, C=N

and C=O. The Raman spectrum is also displayed in the Fig. S1, the D and G peaks can be found at 1423 cm^{-1} and 1610 cm^{-1} , respectively and the obtained NS-CDs has an I_D/I_G ratio of ca. 1.015.

Figure 2. (a) The full scan XPS of NS-CDs. High resolution XPS of C 1s (b), N 1s (c) and S 2p (d) .

As shown in Fig 3a, the UV-Vis absorption spectrum of the products exhibits an absorption peak at ca. 315 nm, which is associated with the $n - \pi^*$ transition of C=O. For further exploring their PL properties, different excitation wavelengths are used to investigate the PL emission of the products in Fig. 3b. The emission wavelength has a strongest intensity at 395 nm and shifts from 430 nm to 480 nm when the excitation wavelength increases from 315 nm to 415nm. According to the analysis of the XPS and TEM pictures, the PL shift of the products would originate from the contribution of differently sized NS-CDs during the nanocrystal growth and the defects on the surface. Interestingly, we find from

the fitting line (in the Fig. 3c) that the relationship between the excitation and emission wavelength can be summarized as the liner regression equation: $y=a*x+b$, therefore, in the range of the excitation wavelength, we can reckon the wanted excitation wavelength in order to gain specific color in applications using the precise function. Fig. 3d shows the Commission Internationale de L'Eclairage (CIE) coordinates of the NS-CDs under a series of excitation wavelengths. The numbers from 1 to 11 (number 4 and 5 are overlapped with each other) in the inset represent the position of the excitation from 315 nm to 415 nm, respectively. With the wavelength increasing from 315 to 415 nm, the colors of the excitation turn from blue to green.

Figure 3. (a) The UV-Vis spectrum of NS-CDs. (b) The PL spectra of NS-CDs under a series of excitation wavelength. (c) The function relationship between the emission and excitation wavelength. (d) The CIE chromaticity coordinate of NS-CDs under a series of excitation wavelength.

The Fig. 4 further explores the properties of the NS-CDs after different metal ions are

added, respectively. It can be recognized that the photoluminescence of the products are quenched by Fe^{3+} ions, which has been previously reported that the fast electron transfer process between Fe^{3+} and carbon dots would cause the luminescence quenching of CDs. According to the dates of XPS and Raman, the N element is mainly existed in the state of pyrrolic-N, and the Fe^{3+} could coordinate with the phenolic hydroxyl groups on edges of CDs¹². What is more, electrons in the excited state of S would transfer to the unfilled orbital of Fe^{3+} , leading to the nonradiative recombination of electron and hole and the fluorescence quenching¹³. In addition, it is the low electronegativity of the sulfur heteroatom on the edge that make the surface electron density of oxygen atoms around sulfur tend to form coordination ibonds with Fe^{3+} , which would further facilitate the photoluminescence quenching¹³. All these phenomena exhibit the synergistic effects of the high content of N and S. The properties of the NS-CDs can help us distinguish the Fe^{3+} from the other ions, which show practical significance in industry and environmental monitoring.

Figure 4. The intensity histogram (a) and emission spectrum (b) of NS-CDs mixing with different heavy metal ions.

4 Conclusion

In summary, the NS-CDs prepared by hydrothermal method exhibits good photo-luminescence and detection properties of metal cations. And the relationship between excitation and the corresponding emission wavelength can be summarized as a linear fitting function. In addition, the as prepared NS-CDs exhibits potential applications in wastewater determination.

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6 References

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