Construction of hydrogen bond mediated nitrogen doped carbon quantum dot fluorescent probe and its application in trace detection of ibuprofen in water

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Abstract. To address the residual pollution of ibuprofen in aquatic environments, this study developed a fluorescent probe based on nitrogen doped carbon quantum dots (NCQDs) as the core material, which can achieve ultra sensitive detection. By optimizing hydrothermal synthesis conditions, NCQDs with uniform particle size (1-4nm) and surface-rich hydroxyl/amino groups were successfully synthesized. FT-IR confirmed their graphitic carbon core structure and surface functional groups. Experiments revealed that ibuprofen formed hydrogen bonds between its carboxylic acid groups and the hydroxyl/amino groups on NCQDs, passivating defect states and suppressing non-radiative recombination, thereby significantly enhancing fluorescence intensity. A linear response was observed within the range of 0.001-0.01mg/L (R2=0.992), the detection limit is 0.14μg/L. This probe offers an efficient and convenient method for trace-level ibuprofen detection in water environments.

Keywords:NCQDs; hydrogen bonding; fluorescence probe.

1. Introduction

Ibuprofen, as an anti-inflammatory drug, has become one of the most frequently detected emerging pharmaceutical contaminants in global aquatic environments due to its widespread use in pain and inflammation treatment[1]. In recent years, with population aging and increasing medical demands, the annual consumption of ibuprofen continues to rise. It enters water circulation systems through human metabolism, pharmaceutical wastewater discharge, and improper drug disposal. Although conventional wastewater treatment processes (such as activated sludge systems) can partially remove ibuprofen (removal rate approximately 50-80%), its high water solubility, persistence, and resistance to degradation still lead to frequent global detection in water bodies. Residual traces have even been found in drinking water sources, raising long-term concerns about ecological safety and human health[2]. Compared with these detection methods, carbon quantum dot fluorescence sensing emerges as a highly attractive alternative, offering numerous advantages including high sensitivity, operational convenience, well-defined structures, excellent stability, rich signal collection capabilities, continuous monitoring potential, and ease of preparation.

Carbon quantum dots (CQDs), as zero-dimensional carbon quantum dots, are characterized by a particle size of 1-10nm and a quasi-spherical structure. Leveraging their nanoscale particle size distribution and biocompatibility[3,4], CQDs exhibit excitation wavelength-dependent photoluminescence (PL) and high-efficiency photoinduced electron transfer capabilities in nanobiotechnology. These properties, combined with their chemically passivated surface structures, collectively establish a low-cytotoxicity smart sensing platform. Through heteroatom doping modification, the density of surface functional groups can be enhanced, leading to significantly improved quantum yields. This strategy further endows the material with responsive fluorescent probe functionalities[5].

2. Experiment

2.1 Preparation of NCQDs

This study successfully synthesized nitrogen doped carbon quantum dots (NCQDs) by hydrothermal method using citric acid and urea as carbon and nitrogen precursors, respectively. To achieve the best synthesis effect, the influence of hydrothermal reaction temperature and time parameters on material properties was systematically investigated, and the preparation process was optimized based on this.

2.2 Quantitative detection of Ibuprofen

Add NCQDs solution to a centrifuge tube and measure its fluorescence spectrum using a fluorescence spectrophotometer in its initial state and after adding different concentrations of Ibuprofen and reacting for 5 minutes. Divide the ratio of the two fluorescence emission peaks before and after adding Ibuprofen as the response value and perform linear regression with the concentration of Ibuprofen to obtain the linear equation of the standard curve. Calculate the detection limit, and the excitation wavelength detected by the fluorescence spectrometer is 365nm.

3. Results and discussions

3.1 Synthesis of NCQDs

By studying the effects of carbon nitrogen source ratio, hydrothermal temperature, and reaction time, the system optimized the synthesis of NCQDs with the best fluorescence performance. The experimental results indicate that the optimal reaction conditions are when the mass ratio of citric acid to urea is 1:2 and hydrothermal synthesis is carried out at 180°C for 10 hours. Extreme hydrothermal temperatures and reaction times can damage the material structure, thereby affecting the fluorescence performance.

3.2 Characterization of NCQDs

Observe the carbon quantum dot powder obtained from the above steps using TEM. The TEM image is shown in Fig. 1 (a), and the observed NCQDs have a nearly spherical shape and uniform distribution. Fig. 1 (b) analyzes the particle size distribution of NCQDs, and the results show that the quantum dots have good dispersibility, with particle sizes concentrated between 1-4nm. After fitting the particle size distribution, the average grain size obtained is (2.3 ± 0.4) nm. The lattice structure characteristics of NCQDs were characterized, and the results showed that its lattice spacing was 0.22nm (inset in Fig. 1 (a)), indicating the presence of sp^2 hybridized carbon in the synthesized NCQDs, proving its graphitization structure.

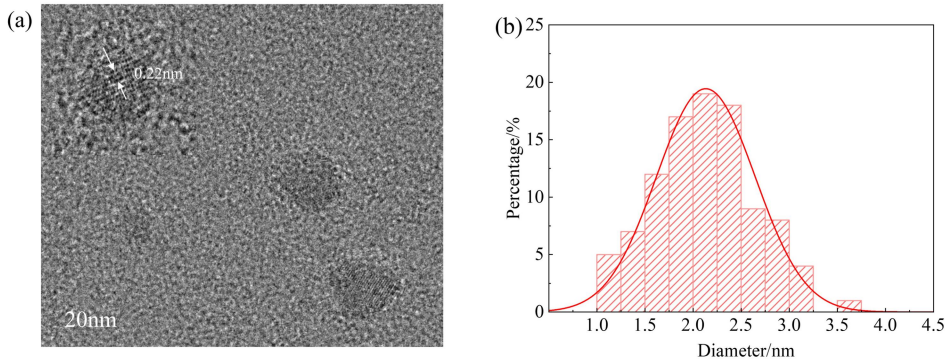

Fig. 1 (a) TEM image of NCQDs (inset shows high-resolution NCQDs); (b) Particle size distribution map of NCQDs

Fig. 2a Infrared spectrum shows the rich distribution of oxygen/nitrogen functional groups on the surface of NCQDs. The stretching vibration peak located at 3008 cm^{-1} can be attributed to the

synergistic stretching vibration of N-H (primary amine) and O-H (phenolic hydroxyl). The appearance of this peak confirms the amino/hydroxyl rich properties of the material surface, which endows NCQDs with good hydrophilicity through surface modification. The characteristic peak at 1544cm^{-1} belonging to the C=C bond in sp^2 hybrid carbon structure, indicating that NCQDs have a graphitized carbon core structure[6]. In addition, the strong stretching vibration peak at 1191cm^{-1} originates from the vibrational mode of the C-O bond[7], while the broad peak at 634cm^{-1} is related to the bending vibration of the CH_2 group[8]. This surface rich oxygen-containing (carboxyl, hydroxyl) and nitrogen-containing (amino) functional group not only enhances the hydrophilicity of NCQDs, but also endows the material with excellent aqueous dispersion stability through electrostatic repulsion, laying the foundation for its application in the field of fluorescent probes[9].

According to Fig. 2 (b), NCQDs fluorescent characteristics reveals an increase with excitation wavelength in the range of 300-380nm, followed by a decrease with further redshift of the excitation light source. The excitation wavelength of 365nm resulted in the maximum fluorescence intensity of NCQDs, indicating that a specific excitation wavelength optimized the photoluminescence performance of NCQDs. Although the spectral distribution under different excitation wavelengths shows a certain degree of similarity, there are also significant differences, and the changes in spectral shape can be attributed to the energy level structure and surface states within NCQDs[10,11].

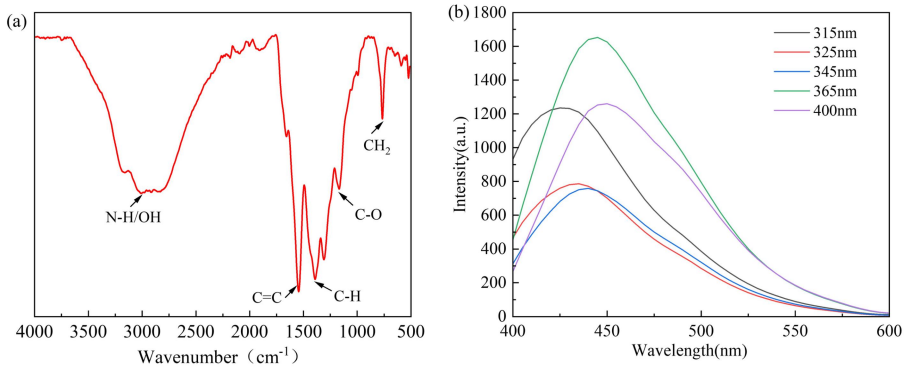

Fig. 2 (a) FT-IR of NCQDs and (b) emission spectra of NCQDs at different excitation wavelengths

This article also analyzed the sensitivity of NCQDs for quantitative detection of ibuprofen, as shown in Fig. 3 (a). When the concentration of ibuprofen increases in a gradient within the range of 0.001-0.01mg/L, the fluorescence intensity of the NCQDs showed a concentration dependent increasing trend. And the fluorescence intensity is relatively stable within the concentration range of 0.001-0.0mg/L. At the same time, it is known that the fluorescence enhancement process induced by ibuprofen does not have a shift in the emission peak. Based on this, the quantitative detection of ibuprofen by NCQDs in this study has been validated (Fig. 3 (b)) . The relative fluorescence intensity ratio F/F_0 is defined within the range of 0.001-0.0mg/L, and the linear relationship between the two can be fitted using the equation: F/F_0=7.3771[ibuprofen]+3.00639, R^2=0.992 and a detection limit of 0.14μg/L. Analysis shows that the linear response range of NCQDs fluorescence sensors to ibuprofen is 0.001-0.01mg/L.

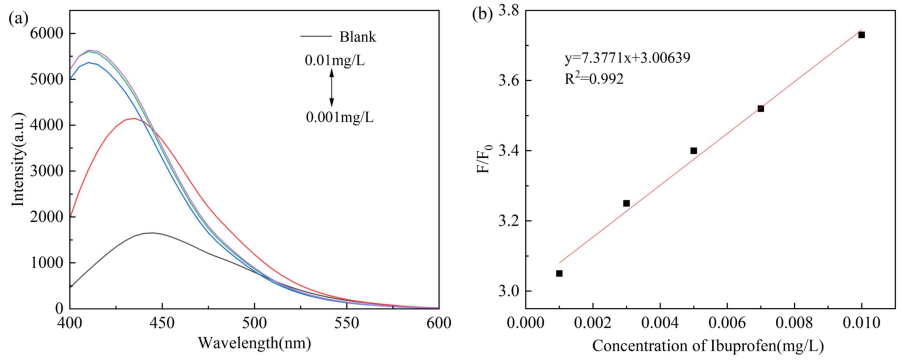

Fig. 3 (a) photoluminescence spectra of NCQDs solutions with different concentrations of ibuprofen added, and (b) linear fitting curves of NCODs solutions with different doses of ibuprofen added

3.3 Fluorescence enhancement mechanism of NCQDs

According to the Fourier transform infrared spectrum of the mixed solution of NCQDs and ibuprofen, as shown in Fig. 4, it can be seen that the characteristic peak of the O-H bond is in the range of 3500-3100cm^{-1}, and the peak shape becomes wider and the peak intensity increases, confirming the generation of hydrogen bonds. The carboxylic acid groups of ibuprofen form hydrogen bonds with the hydroxyl groups of NCQDs; this interplay induces an ordered arrangement of surface functional groups and significantly suppresses surface defect formation[12,13]. Defect states are usually used as non radiative recombination centers, and their reduction can reduce energy loss, thereby enhancing the fluorescence intensity of NCQDs.

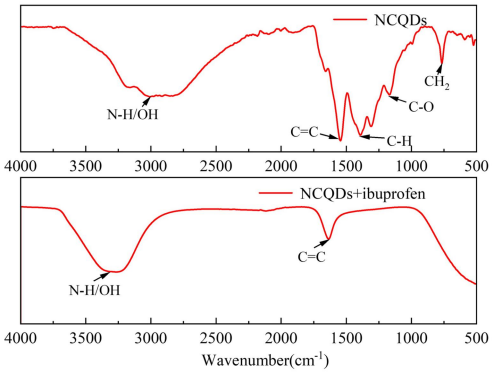

Fig. 4 FT-IR spectra before and after adding ibuprofen to NCQDs aqueous solution

4. Conclusions

This study developed a novel NCQDs fluorescence sensor that achieves highly sensitive and rapid detection of ibuprofen pollutants in aquatic environments. NCQDs optimized by hydrothermal method have uniform particle size (1-4nm), surface functional groups, and graphitized structure, significantly improving fluorescence performance. Ibuprofen forms hydrogen bonds with the surface of NCQDs through carboxylic acid groups, inhibiting non radiative recombination and increasing fluorescence intensity by about three times. The detection limit of the probe is 0.14μg/L, with a linear range of 0.001-0.01mg/L (R^2=0.992). It has high sensitivity and easy operation, providing an efficient solution for trace monitoring of ibuprofen in water.

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