Preparation and Application Studies of Fluorescent Sulfur Quantum Dots

Yuexiu Liu

Lingnan Normal University,Zhanjiang, Guangdong,524048

Abstract: Sulfur quantum dots have been widely used in fluorescence detection, bioimaging, and sensing due to the advantages of simple preparation, biocompatibility, good luminescence performance, and low toxicity. An overview of the the preparation methods of SQDs for applied research. The preparation methods of SQDs can be categorized into bottom-up and top-down methods, in which the top-down method is more widely used in the research and the fluorescence quantum yield of synthesized sulfur quantum dots is higher. Finally, the urgent problems to be solved in the synthesis and application of sulfur quantum dots are discussed, and the future research directions are envisioned.

Keywords: Sulfur Quantum Dots; Preparation Methods; Applied Research

1. Introduction

Sulfur quantum dots (SQDs) are novel metal-free sulfur nanomaterials with particle size less than 10 nm, consisting of discrete quasi-spherical singlet sulfur nuclei and surface ligands.[1] which consists of discrete quasi-spherical monolithic sulfur nuclei and surface ligands, exhibiting unique fluorescent properties, non-toxicity, hydrophilicity, luminescence, and high stability with ease of functionalization, and have attracted widespread attention[2] It has received wide attention. Compared with quantum dots such as silicon and carbon, elemental sulfur is often used as an antibacterial or antifungal agent due to its unique bactericidal properties and its wide distribution in nature at a low price[3] . In addition, using SQDs as fluorescent signals as response objects has a broad application prospect in detecting metal ions environmental pollution. This paper reviews the different preparation methods of SQDs and their progress in the field of applied research, and analyzes the effects of different synthesis methods on the performance of SQDs.

2. SQDs preparation method

With the continuous research, there are several methods for synthesizing SQDs. There are two main types of synthesis methods reported so far: (1) bottom-up synthesis method and (2) top-down synthesis method. The details are shown in Fig.

2.1 Bottom-up synthesis

In 2014, Li et al. prepared SQDs with blue fluorescence for the first time using CdS and ZnS quantum dots as precursors at room temperature and pressure[2] . The method used etching to dissolve CdS QDs or ZnS QDs dispersed in cyclohexane and to oxidized to S. The prepared SQDs have good photostability, excellent water solubility, and low toxicity, but low PLQY (0.549%), long reaction time, and complicated operation limit their wide application. 2020 Arshad et al. used and PEG-modified SQDs were prepared as raw materials under the environment of polyethylene glycol 400 (PEG) and NaOH[3][4]. This method broadened the choice of precursors for SQDs and the synthesized SQDs had better dispersion and stability, and the PLQY was enhanced to 2.5%, but it still could not meet the demand for high-brightness fluorescent materials.

2.2 Top-down synthesis

The top-down method is to prepare SQDs directly by oxidative etching of sublimated sulfur powder, which is widely used in current scientific research, mainly including the assembly-fission method, hydrogen peroxide-assisted method, etc. In 2018, Shen et al. reported for the first time an “assembly-fission” mechanism, which successfully explains the synthesis mechanism of SQDs.[4] . This method used PEG-400 as a passivator, and dissolved, assembled, and fissioned S powder in NaOH environment by changing the reaction duration, and successfully obtained SQDs with different sizes and tunable fluorescence emission, but with a PLQY of only 3.8%.In 2019, Wang et al. improved the method by using the oxidative etching of S powder[5] by adjusting the concentration and changing the heating duration, similar advantages to the above method could also be achieved, and the PLQY was increased to 23%.

However, the above two methods have the problem of long reaction time, and in order to shorten the reaction time, research teams have improved the preparation method of SQDs. In 2019, zhang et al. reported a method of chemical etching of S powder using ultrasonic assistance[6] which reduced the reaction time to within 5 h, and the obtained SQDs had advantages such as high dispersibility, but the PLQY was only 2.1%. Xiao et al. successfully prepared SQDs using a one-step hydrothermal method with a mixed solution of S powder, PEG-400, and NaOH water as the raw material, which greatly reduced the reaction time to within 4 h[1] The reaction time was greatly reduced to less than 4 h. Using the same raw materials, zhou et al. reported the synthesis of highly fluorescent SQDs by the synthesizing highly fluorescent SQDs under the atmosphere of a new method[4] Using the same raw material, zhou et al. reported a new method to synthesize highly fluorescent SQDs by synthesizing them in an atmosphere, which shortened the reaction time to 10 h and prepared SQDs with a yield of 5.08% for the first time.

To improve the PLQY of SQDs, in 2020, Song et al. reported a new method of synthesizing highly fluorescent SQDs by a new method to synthesize highly fluorescent SQDs under the atmosphere[2] The key to synthesizing SQDs is that the It is possible to oxidize oxidized to S, which makes the reaction yield of elemental sulfur as high as 5.08% far more than other synthesis methods (1%), and the SQDs can reach 21.5%, but it is difficult to realize the market demand due to the high purity of oxygen required for the reaction and the high experimental requirements.In 2020, Li et al. proposed an assisted precipitation etching method[1] which prepared SQDs with a PLQY of 32.8%. However, due to potential toxicity, it failed to be widely used in biological and environmental fields. In the same year, Hu et al. developed a new microwave-assisted method for the preparation of SQDs[2] with a PLQY as high as 49.25%. In the following year, Sheng et al. innovatively proposed ultrasound-microwave-assisted and chemical etching of SQDs[3] which further shortened the synthesis time to 2 h and increased the PLQY of SQDs to 58.6%. Subsequently, in 2022, Gao et al. developed a successful hydrothermal method for the preparation of SQDs based on ethylenediamine solvent[6] In 2022, Gao et al. developed a successful hydrothermal method based on ethylenediamine solvent for the preparation of SQDs, which was able to obtain SQDs emitting strong blue fluorescence with a PLQY as high as 87.8% in an autoclave for 5 h. The reaction was performed in a high pressure reactor. Compared with other synthesis methods, this method is simplified and easy to operate, and the SQDs can be purified and collected by directly adding ethanol, and the resulting SQDs have low toxicity, good photostability and excellent water solubility, which have broad application development in industrialization.

3. SQDs applied research

Based on the influence of analytes on the detection of fluorescent properties of SQDs, the researchers developed applications of SQDs in bioimaging, luminescent materials, catalytic activity, electrochemical sensing, fluorescence sensing, etc[7] . Among them, fluorescence sensing has become a popular research field with prominent applications due to its advantages of good stability, high sensitivity, low detection limit, easy operation and low cost. According to the reported fluorescence sensor applications of SQDs, metal ions can change the surface groups or structure of SQDs, resulting in the fluorescence signal burst, enhancement, and fluorescence resonance energy shift of SQDs, based on this mechanism, researchers have established the , Based on this mechanism, researchers have successively established Based on this mechanism, researchers have successively established the detection methods for more than 10 kinds of metal ions[6] Based on this mechanism, researchers have successively established more than 10 metal ion detection methods, including

Most of the metal ions will weaken the fluorescence signal of SQDs, i.e. static burst or dynamic burst.[6] Based on this principle, Li et al. successfully constructed a fluorescent probe for selective detection of SQDs.[1] and when the concentration is in the region of 0~0.003%, there is a good linear relationship, which indicates that the method can be used for the real samples in the high sensitivity detection.

However, some metal ions not only do not burst the fluorescence of SQDs, but also enhance the fluorescence intensity due to the induced aggregation effect of SQDs. By reducing the consumption of SQDs excitation energy by non-radiative pathways to enhance the fluorescence[3] Chen et al. constructed a linear range ( ) with a low detection limit ( ) of SQDs and the anti-interference test found that the SQDs had a high selectivity for the SQDs with high selectivity and sensitivity. Since the contaminated water bodies cannot be recognized, the SQDs can be used to detect contaminated water is unrecognizable and will cause many diseases if residents drink it for a long time, this fluorescent probe can contribute to the defense of drinking water health.

The above two types of single fluorescence emission detection can accomplish the detection of trace ions, but the detection fluctuates greatly under the influence of external factors, which causes interference and errors in the ion detection work. Since then, a method using dual fluorescence emission signals to determine ions has been developed, which has a self-calibration function compared with single fluorescence emission detection.[6] Zhang et al. found that In the presence of SQDs, the fluorescence of SQDs is burst due to internal filtration effect, but the fluorescence intensity of carbon quantum dots (CQDs) is enhanced, and the color of the system changes from colorless to dark yellow.[3] The color of the system changed from colorless to dark yellow. The detection limit of this method was 31 nmol/L. Comparing with the lowest detection limit of single fluorescence emission (47 nmol/L), it was concluded that the dual fluorescence emission probe was more accurate.

4. Conclusion

SQDs are quite promising fluorescent nanomaterials for research due to their unique optical properties and good biocompatibility. Compared with AAS, AFS, and ICP-MS detection methods, the detection method of SQDs is easy to operate, simple in principle, inexpensive, and highly sensitive, which has great application prospects in practical analytical detection work. However, compared with the traditional quantum dots such as C, Si, ZnS, etc., the current SQDs have the problems of fewer preparation methods, longer time-consuming, lower fluorescence quantum yield, and the emission color is limited to blue-green. As of now, neither the top-down nor bottom-up method can simultaneously take care of PLQY and synthesis efficiency. Therefore, the development of new SQDs preparation and surface modification techniques to further shorten the reaction time and improve the PLQY is a critical issue to be addressed in the development of SQDs. Regarding the future research of SQDs, expanding the reaction precursors, changing the synthesis conditions, and designing purified preparation routes are the research directions that researchers tend to extend at present. It is foreseeable that through the unremitting efforts of the research team, the results of process optimization of SQDs will greatly promote the development of SQDs in practical applications.

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About the author:Yuexiu Liu(2002.12-), Female, Han nationality, native of Zhanjiang, Guangdong, Lingnan Normal University, Bachelor's Degree, Fluorescent Sulfur Quantum Dots.