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TUNABLE PHOTOLUMINESCENCE OF METAL ION DOPED ZINC SULFIDE QUANTUM DOTS

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Compared with common quantum dots, the doped ZnS quantum dots (ZnS QD) have outstanding properties in luminescence, electricity and other fields and have became research focus in material science. In this research, ZnS:Na^+,Mg^{2+} QD, ZnS:Na^+,Cr^{3+} QD and ZnS:Mg^{2+},Cr^{3+} QD were prepared by aqueous-phase synthesis. The quantum dots were analyzed and characterized by XRD, TEM, fluorescence spectra and IR spectra. The results showed that double-doping didn't have effect on the structure of ZnS QD. The ZnS QD approximated sphere with reunion phenomenon and had obvious lattice structure. The doping of metal ions could regulate the fluorescence properties of the ZnS QD.

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Keywords: ZnS quantum dots, Aqueous-phase synthesis, Luminescence property

1. Introduction

Compared with common quantum dots, the doped ZnS quantum dots have outstanding properties in luminescence, electricity and other fields and have became research focus in material science [1]. In the luminescence properties, the doped ZnS quantum dots have intrinsic quantum dots' excellent luminescence properties [2]. What's more, it can effectively control and intensify the properties. Such as the excited lifetime become longer, luminescence properties become stable, spectral range become wider. The most importance is that because of stokes shift the ZnS quantum dots can avoid quenching phenomenon which is caused by self-absorption. So the doped ZnS quantum dots have more and more important application value in electroluminescence, fluorescence labeling and other fields.

The luminescence intensity of the ZnS quantum dots is limited. By adding other ions, the luminescence intensity of the quantum dots can be effectively improved. ZnS:Fe^{3+} QDs were synthesized through chemical co-precipitation method by Shamsipur [3] and Rajabi [4]. And ZnS:Fe^{3+} QDs were prepared for photodecolorization of methyl violet or malachite green, as a model dye, under UV light irradiation. In Chantada's article [5], Mn-doped ZnS quantum dot was applied to cocaine screening in oral fluid and serum.

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In this research, ZnS:Na^{+},Mg^{2+} QD, ZnS:Na^{+},Cr^{3+} QD and ZnS:Mg^{2+},Cr^{3+} QD were prepared by aqueous-phase synthesis. And the phase composition, micromorphology and fluorescence properties of ZnS QD were characterized and analyzed. Furthermore, the mechanism of metal ions doping control on the luminescence properties of ZnS quantum dots was discussed.

2. Materials and methods

2.1Materials

Zinc acetate ($(CH_3COO)_2Zn•2H_2O$, AR) was purchased from Tianjin Zhiyuan Chemical Reagent Co. Ltd., China. Sulfocarbamide (H_2NCSNH_2, AR) was purchased from Tianjin Tianli Chemical Reagent Co. Ltd., China. Sodium acetate (CH_3COONa, AR), Magnesium acetate ($(CH_3COO)_2Mg•4H_2O$, AR) and Chromium acetate ($(CH_3COO)_3Cr$, AR) were purchased from Harbin Xinchun Chemical Plant, China. And Caustic soda (NaOH, AR) and Sodium sulfide ($Na_2S•9H_2O$, AR) were purchased from Tianjin Henxing Chemical Reagent Co. Ltd., China. All chemicals were of analytical reagent and used directly without further purification.

2.2 Preparation

A certain amount of zinc acetate and sulfocarbamide were dissolved in deionized water. Then a certain amount of metal ions were added to the solution. The solution was stirred evenly on the constant temperature magnetic stirrer. Then using 1M NaOH solution to adjust the pH of the reaction system to 13. The solution was continuously stirred for 30min. The solution and Na_2S were transferred to flask, and the ZnS QDs were obtained by stirring continuously for 5h under the N_2 atmosphere and 80℃ water bath.

2.3 Characterization

The phase of the product was identified by X-ray diffraction (XRD, PANalytical X-Pert PRO MPD, Netherlands) with Cu-Kα radiation. Morphological features of the samples were observed using transmission electron microscopy (TEM, JEOL JEM2100, Japan). Photoluminescence (PL, Shimadzu RF-5301PC, Japan) spectra were measured at room temperature using a 150 W xenon lamp as the excitation source.The composition of the prepared samples were further tested by fourier transform infrared spectroscopy (FTIR, Thermo Nicolet 360, America).

3. Result and discussion

3.1 The Analysis of Phase and Structure

Fig. 1 was the XRD patterns of ZnS quantum dots doped with metal ions. The samples were (a) ZnS:Na^{+},Mg^{2+}; (b) ZnS:Na^{+}, Cr^{3+}; (c) ZnS:Mg^{2+},Cr^{3+}, respectively.

As can be seen from Fig. 1, the diffraction peaks of the samples were in accordance with the standard PDF card (01-0792), which proved that the synthesized ZnS was cubic β-ZnS structure. At the same time, it can be observed that the position of the diffraction peaks corresponding to the (220) crystal plane and (311) plane of the samples were right shifted with the

position of the standard card, to a certain extent. This phenomenon indicates that the interplanar spacing of (220) crystal plane and (311) crystal plane was smaller, which may be attributed to the metal ions entering the ZnS lattice.

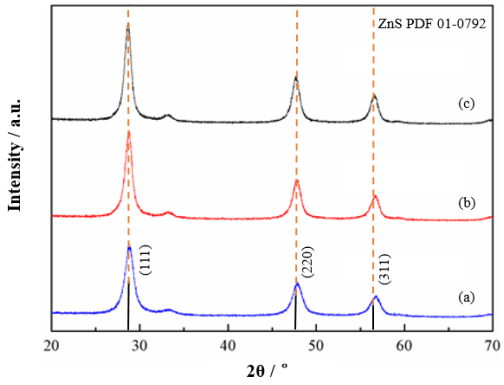

Fig.1. XRD patterns of ZnS quantum dots doped with metal ions.

Fig. 2 was the IR spectrum of ZnS quantum dots doped with metal ions. It was observed in Fig. 2 that -OH, C≡N, -NO_2,C-N, C-O and other functional groups exist on the synthesized ZnS quantum dots, and the functional groups of C and N elements were derived from thiourea.

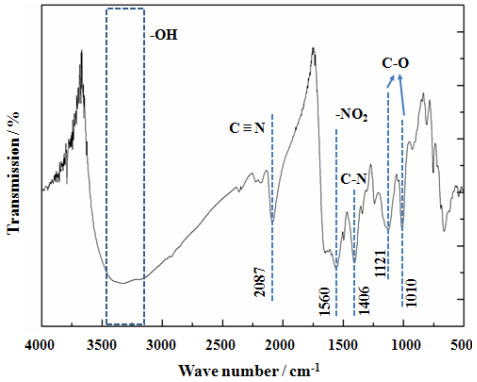

Fig. 2. IR spectrum of ZnS quantum dots doped with metal ions.

3.2 Micro-morphology characterization

Fig. 3 was TEM images of ZnS QD. (A. ZnS:Na^{+},Mg^{2+}; B. ZnS:Na^{+}, Cr^{3+}; C. ZnS:Mg^{2+},Cr^{3+})

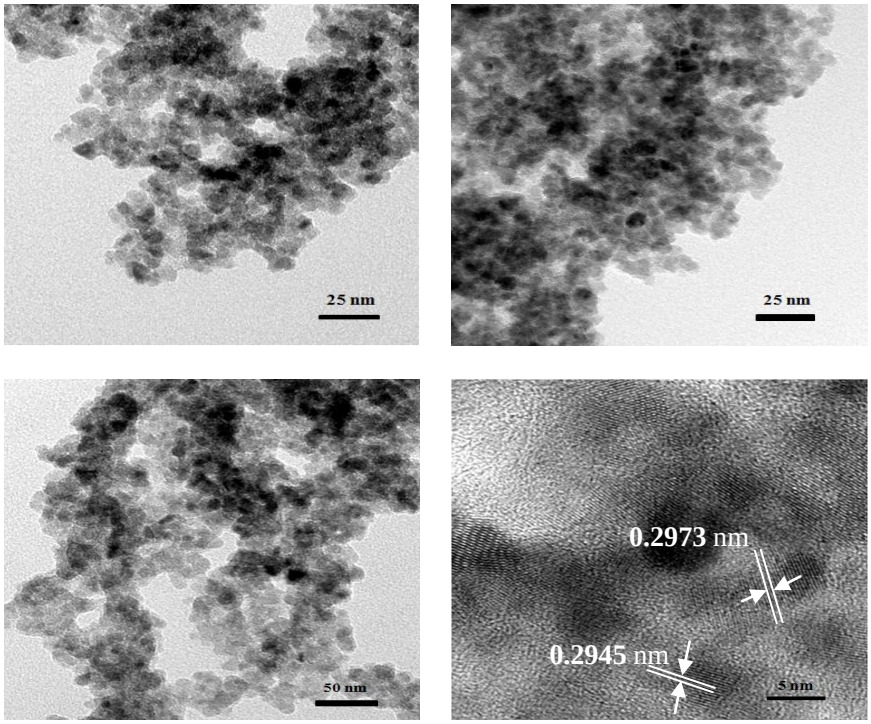

Fig. 3. TEM images of ZnS quantum dots doped with metal ions.

It can be seen from the Fig. 3 that the quantum dots existed in the field of vision, and the dispersion was not good. The shape of a single quantum dot was approximately spherical.

3.3 Fluorescence regulation of ZnS:Na^{+},Mg^{2+} QD

Fig. 4 was emission spectrum of ZnS:Na QD and excitation spectrum of ZnS:Mg QD. It can be seen from the graph that two spectral curves overlap between 425nm and 460 nm, which indicates that the double doping of Na^{+} and Mg^{2+} will lead to energy transfer. The occurrence of energy transfer made it possible to regulate the fluorescence of the quantum dots.

Fig. 5 was emission spectra of ZnS:Na^{+},Mg^{2+} QD. Here, the excitation wavelength was 420nm. The doping amount of Na in the tested samples was 1%, and the amount of Mg was 0.5%, 0.8%, 1.0%, 1.3% and 1.6%. Under the above conditions, the emission peaks of the quantum dots were located in the green light region. Moreover, the change of the luminescence intensity with the amount of Mg doping was shown in Fig. 5.

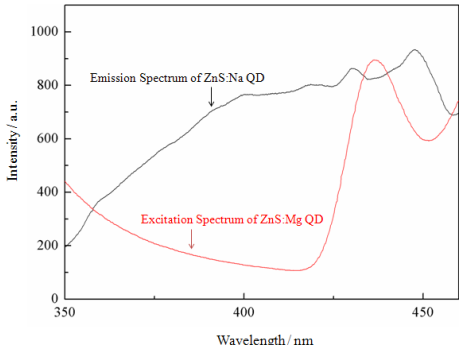

Fig. 4. The emission spectrum of ZnS:Na QD and excitation spectrum of ZnS:Mg QD.

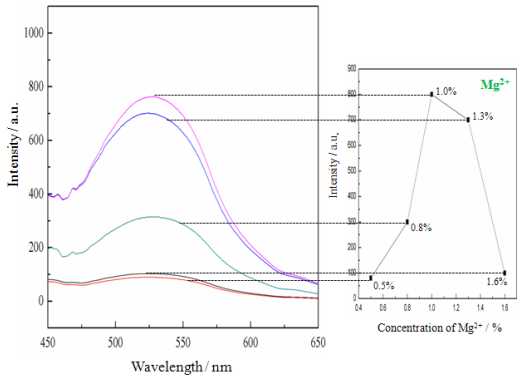

Fig. 5. The emission spectra of ZnS:Na^+,Mg^{2+} QD.

3.4 Fluorescence regulation of ZnS:Na^+,Cr^{3+} QD

Fig. 6 was emission spectrum of ZnS:Cr^{3+} QD and ZnS:Na^+,Cr^{3+} QD. From Fig. 6, it can be seen that the introduction of Na^+ led to a red shift of the emission peak of ZnS:Cr^{3+} QD. The reason for this phenomenon was that the Na^+ radius is smaller than that of Cr^{3+}. After doping, the partial Cr^{3+} position was replaced, and the cell contraction occurred, resulting in the reduction of the distance between the center ion and the coordination ion. According to the law of the energy level splitting energy and the bond length inversely proportional to the crystal field, the intensity of the crystal field will increase and eventually lead to the red shift of the spectrum.

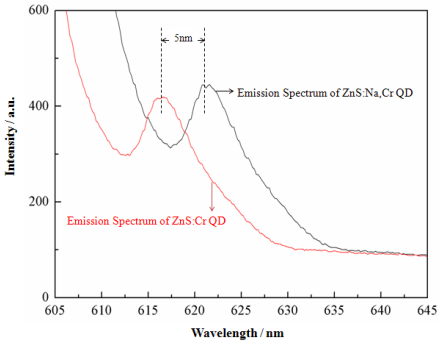

Fig. 6. The emission spectrum of ZnS:Cr^{3+} QD and ZnS:Na^+,Cr^{3+} QD.

Fig. 7 was emission spectra of ZnS:0.01Na^+,$x$$Cr^{3+}$ QD (x=0.5%, 0.8%, 1.0%, 1.3%, 1.6%). The peak position of the emission peak was 621 nm, which belonged to the red light region. With the difference of Cr doping concentration, the luminescence intensity of ZnS:Na^+,Cr^{3+} QD changed. It may be caused by the change in the size of the cell.

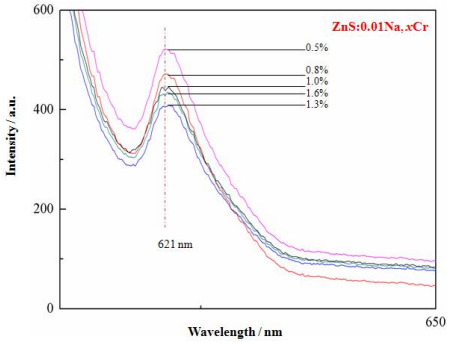

Fig. 7. The emission spectra of ZnS:0.01Na^{+},xCr^{3+} QD (x=0.5%, 0.8%, 1.0%, 1.3%, 1.6%).

3.5 Fluorescence regulation of ZnS:Mg^{2+},Cr^{3+} QD

Fig. 8 was emission spectrum of ZnS:Mg QD and excitation spectrum of ZnS:Cr QD. It can be seen from the graph that two spectral curves overlap between 525nm and 550 nm, which indicates that the double doping of Mg^{2+} and Cr^{3+} will lead to energy transfer. The occurrence of energy transfer made it possible to regulate the fluorescence of the quantum dots.

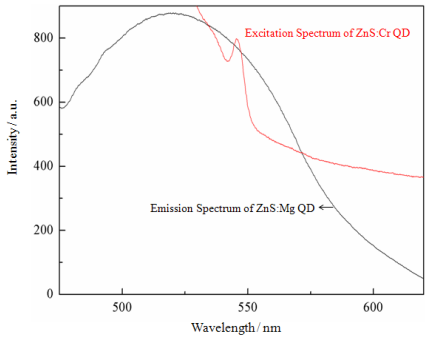

Fig. 8. The emission spectrum of ZnS:Mg QD and excitation spectrum of ZnS:Cr QD.

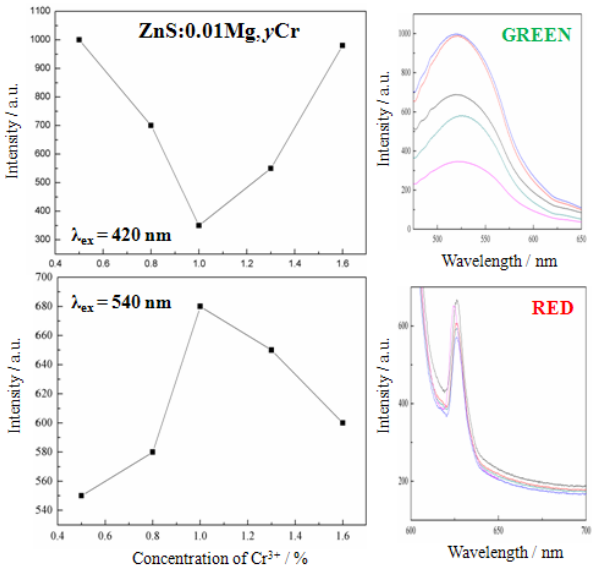

Fig. 9. The emission spectra of ZnS:Mg^{2+},Cr^{3+} QD.

Fig. 9 was the emission spectra of ZnS:Mg^{2+},Cr^{3+} QD. It showed the fluorescence tunability of ZnS:Mg^{2+},Cr^{3+} QD. When the excitation wavelength was 420nm, green light emission can be detected. And when the excitation wavelength was 540nm, the light was red.

4. Conclusions

The ZnS quantum dots prepared by the method of aqueous-phase synthesis were spherical. And it was observed that -OH, C≡N, -NO_2, C-N, C-O and other functional groups exist on the synthesized ZnS QD.

The color and intensity of the ZnS quantum dots can be adjusted by changing the types of doped ions. ZnS:Na^{+},Mg^{2+} QD emits green light under the excitation of 420nm laser. ZnS:Na^{+},Cr^{3+} QD emits red light under the excitation of 540nm laser. And ZnS:Mg^{2+},Cr^{3+} QD was capable of emitting green and red light, respectively.

Acknowledgment

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