

STUDY ON STRUCTURAL AND LUMINESCENCE PROPERTIES OF ZnS:Mg²⁺ QUANTUM DOTS SYNTHESIZED WITH AQUEOUS METHOD

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Using thiourea as surface modifier, ZnS:Mg²⁺ quantum dots are successfully prepared by aqueous phase method. X-ray diffractometer, TEM and fluorescence spectrophotometer are used to analyze structure properties and luminescent properties of ZnS:Mg²⁺ quantum dots. At the same time, by the infrared absorption spectrum, we analyze the formation mechanism of ZnS:Mg²⁺ quantum dots. The results show that the as-obtained samples are cubic sphalerite structures and are approximate to spheres. They distribute uniformly but have adhesion phenomenon. The measures of quantum dots are about 4nm. The samples emit green light at 525nm. The best preparing conditions are that the doping concentration of Mg²⁺ is 1.5%, thiourea/ZnS is 1.5:1 and pH value is 13.

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1. Introduction

ZnS quantum dots have obvious quantum size effect, surface effect and dielectric confinement effect. In the fields of emitting diode^[1], FPD^[2], fluorescence printing ink^[3] and biomarker^[4], ZnS quantum dots show huge utilization potentiality. In recent years, experts have invented various kinds of methods of preparing ZnS quantum dots. For example, Wang Jun^[5] synthesized smaller diameter ZnS quantum dots successfully with ethylene glycol and water as reaction solvent through solvothermal method. Li Yao^[6] synthesized size controllable ZnS quantum dots with CS₂ as the source of sulfur through the micro-emulsion method. However, most of ZnS quantum dots prepared with these methods are non-water-soluble. In the applications of biomedical, fluorescent ink and environmental monitoring, we require that ZnS quantum dots must be water-soluble. Aqueous phase method just fit the bill, so preparing ZnS quantum dots with this method has become the researching emphasis. Pure ZnS materials have low luminous efficiency and high resistance due to the mixed effect between irregular particles. So when being excited, ZnS may decompose. The excitation wavelength range of pure ZnS materials is limited, so the

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largest exciting wavelength is about 340 nm at room temperature^[7]. Its ability of shock resistance needs to improve. As a result, improving the luminescent property of ZnS quantum dots turns into our researching emphasis.

Reviewing the development process of ZnS quantum dots we find that we can improve the luminescent property by doping ions. In ZnS substrates, the main doping ions include transition metal ions, rare earth ions and other ions. Among them, the researches of ZnS quantum dots doped with Mn^{2+} 、 Cu^{2+} and Ga^{2+} are more than others. On the contrary, the Mg^{2+} -doped ZnS quantum dots are studied rarely.

So in order to further study ZnS nanometer materials' potential performance, it is necessary to study the ZnS quantum dots doped with different positive ions. The forbidden band widths of Mg^{2+} and ZnS are 7.9eV and 3.6eV respectively. When Mg^{2+} is doped in ZnS quantum dots, the forbidden band width of ZnS would be increased. This phenomenon is conducive to improve luminescent property. In this paper, we use $(CH_3COOH)_2 Zn \cdot 2H_2O$, $Mg(CH_3COOH)_2 \cdot 4H_2O$ and $Na_2S \cdot 9H_2O$ as the raw materials and use thiourea as surface coated agent. At last, we successfully prepare the water-soluble Mg^{2+} -doped ZnS quantum dots photoluminescence materials. We analyze the structures and morphologies before and after doping Mg^{2+} , and the effects of different doping concentrations and different surface coated agent concentrations on luminescent property.

2. Experimental details

The process of preparing pure ZnS quantum dots: $(CH_3COOH)_2 Zn \cdot 2H_2O$ and thiourea that have been weighed are dissolved with 75ml deionized water. After mixing uniformly, the 1mol/L NaOH is used for adjusting the pH value until the pH is 10. Flask with three necks, condenser pipe and water bath kettle are putted together, and this set of equipment is connected with nitrogen gas for 20 minutes. $Na_2S \cdot 9H_2O$ and mixed solution are putted in the flask with three necks, after reacting under the condition of 100°C water bath for 4 hours, we get ZnS quantum dot hydrosols. Then the products are centrifuged to eliminate supernatant and get white precipitates. The white precipitates are washed with distilled water and anhydrous ethanol for several times and are dried at 90°C for 5 hours. Finally, the products are grinded to ZnS quantum dot powders.

In order to prepare Mg^{2+} -doped ZnS quantum dots, after dissolving $(CH_3COOH)_2 Zn \cdot 2H_2O$ and thiourea, $Mg(CH_3COOH)_2$ needs to be putted in the mixed solution. The remaining steps are the same.

The structure of ZnS quantum dots is established by X-ray diffractometer (XRD) and the morphology of the quantum dots are observed by transmission electron microscope (TEM). The photoluminescence property of the quantum dots is analyzed by fluorescence spectrophotometer. The formation mechanism of quantum dots is analyzed by infrared absorption spectrum.

3. Results and discussion

3.1 Structural properties

The XRD patterns of pure ZnS and 1% Mg^{2+} -doped ZnS quantum dots are presented in Fig.1. Comparing with standard card JCPDS(NO.05-0566), these three diffraction peaks

correspond to the (111)、(220) and (311) lattice planes. This shows that these two samples belong to cubic sphalerite structures and doping Mg^{2+} has no effect on the structure of ZnS quantum dots.

Three diffraction peaks in Fig.1 have obvious widened phenomenon. This shows that the two samples have quantum size effect. In (111) lattice plane, the diffraction peaks of Mg^{2+} -doped ZnS and pure ZnS quantum dots are located at 28.94° and 28.85° respectively. It can be seen that the diffraction peak of ZnS: Mg^{2+} moves to the right about 0.09° . It is because that the radius of Mg^{2+} is smaller than it of Zn^{2+} , this leads to decreasing the interplanar spacing of ZnS quantum dots. So we can see that Mg^{2+} takes the place of Zn^{2+} and enters into the inside of ZnS lattice [8]. At the same time, the diffraction peak of ZnS: Mg^{2+} quantum dots is sharper than that of pure ZnS quantum dots. It can be concluded that doping Mg^{2+} improves the crystallization extent of ZnS quantum dots.

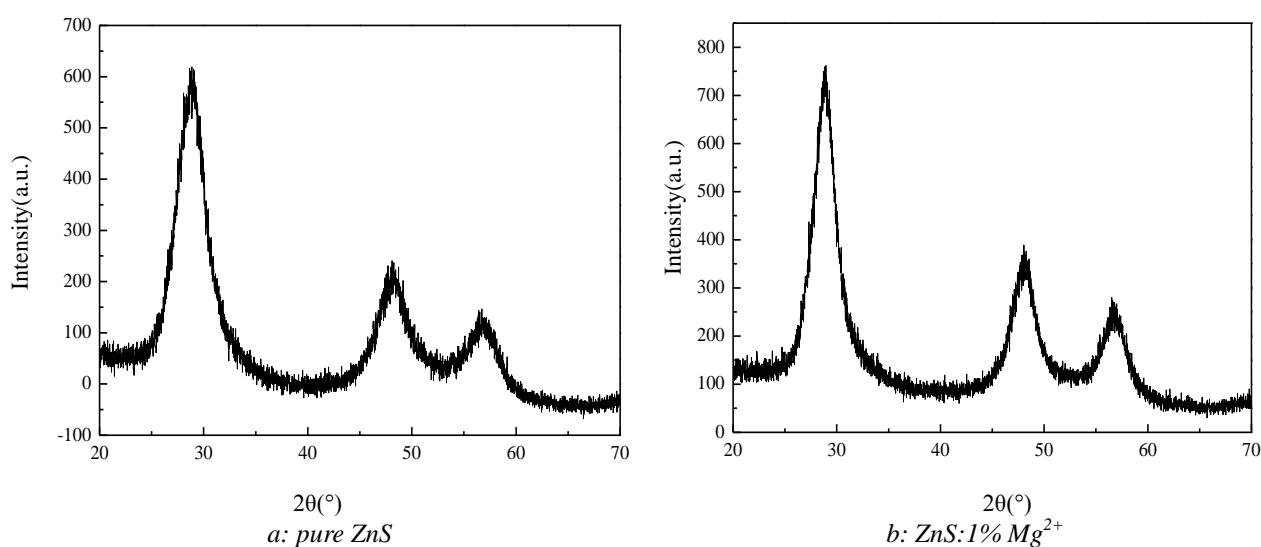


Fig.1: The XRD patterns of pure ZnS and 1% Mg^{2+} -doped ZnS quantum dots

3.2 Morphology properties

TEM images of pure ZnS and ZnS: Mg^{2+} quantum dots are shown in Fig.2.

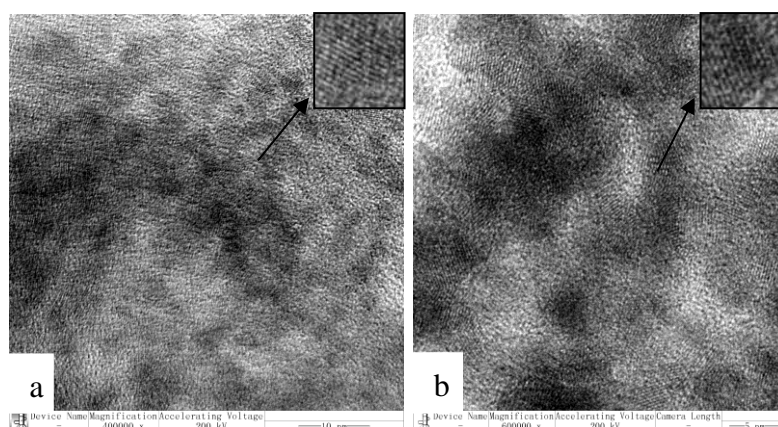


Fig.2: TEM images of pure ZnS and ZnS: Mg^{2+} quantum dots
a: pure ZnS *b: ZnS: Mg^{2+}*

From image a and b, we can see that they are approximate to spheres and distribute uniformly. The small images at top right corner show that the quantum dots have lattice fringe. Some darker parts of pictures reflect that particles have adhesion phenomenon. It is mainly because of solvent evaporation. The measures of pure ZnS and ZnS:Mg²⁺ quantum dots are 4nm and 4.5nm respectively. After doping Mg²⁺, the quantum dots are bigger than before. It is accord with XRD patterns.

3.3 Luminescent properties

The emission spectra of different concentrations of Mg²⁺ doping are presented in Fig.3.

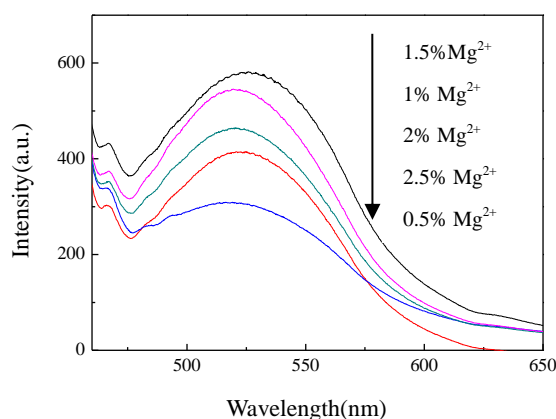


Fig.3: The emission spectra of different concentrations of Mg²⁺ doping

The excitation wavelength is 420nm. From the spectras we can see two emission peaks. The low peak is located at 467nm and the high peak is located at 525nm. The left peak is due to the defect emission of Zn²⁺ of deep electron hydrazine, emitting weak blue light ^[9]. The right peak is due to the impurity level emission of Mg²⁺, emitting strong green light. When doping concentration is 0.5%, the luminous intensity is the weakest. With the increase of doping concentration, the luminous intensity improves obviously. When the doping concentration is 1.5%, the luminous intensity reaches a maximum. This is because doping Mg²⁺ reduces the dangling bonds and unsaturated bonds of the surface of ZnS and repairs the defect states^[10]. Increasing the doping concentration adds the surface radiative recombination luminescence centers, thus improves the luminous intensity. When continue increasing Mg²⁺, the intensity reduces. It's because that superfluous Mg²⁺ make the particle diameter smaller, surface area bigger, the particle surfaces appear lots of dangling bonds and unsaturated bonds and form surface defect states. These phenomenon increase surface nonradiative recombination luminescence centers, thus reduce the luminous intensity^[11].

The emission spectra of different doping proportions of thiourea/ZnS are presented in Fig.4.

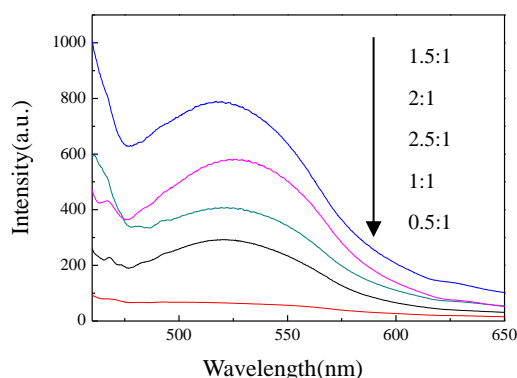


Fig.4: The emission spectra of different doping ratios of thiourea/ZnS

The starting proportion is 0.5:1. When it reaches 1.5:1, the luminous intensity is the highest and the emission peak is located at 525nm. Continue increasing the doping proportions, the luminous intensity goes down and when the proportion is 2.5:1, it is the lowest. This is because the thiourea is too little that it can't give ZnS quantum dots effective surface modification, therefore, it causes agglomeration of quantum dots and influences luminescent properties. When thiourea is too much, most of the Zn precursors and S precursors exist as RS-Zn-SR and S monomers, making the chemical chain reaction of ZnS can't continue and luminous intensity go down^[12]. We can conclude that the best doping proportion is 1.5:1.

The emission spectra of ZnS:Mg²⁺ quantum dots in different pH value are presented in Fig.5.

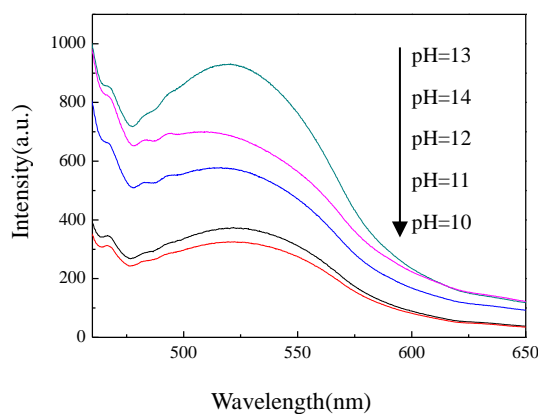


Fig.5: The emission spectra of ZnS:Mg²⁺ quantum dots in different pH

The range of pH value is from 10 to 14. With the increasing of pH value, the emission intensity increases until pH value is 13. However, continue increasing pH value, the intensity decreases. The reason is that when pH value is lower than 13, OH⁻ ions are not enough, so they affect the recombination of Mg²⁺ and thiourea and reduce luminous intensity of Mg²⁺ impurity level. When pH value is higher than 13, the growth of quantum dots speeds up and make the quantum dots have low crystallinity and appear a large number of surface defects^[13]. As a result, the luminous intensity reduces.

3.4 ZnS:Mg²⁺ quantum dots infrared spectral analysis

Fig.6 is the infrared absorption spectrum of ZnS:Mg²⁺ quantum dots. From it we can see that the stretching vibration peak located at 3313.61cm⁻¹ belongs to N—H group and it located at 1406.38cm⁻¹ belongs to C—N group^[14]. The two groups come from thiourea. It shows that thiourea has coated on the surface of ZnS:Mg²⁺ quantum dots. The absorption peak located at 1560.72cm⁻¹ is the asymmetrical stretching vibration peak of nitro, showing that a part of thiourea reacts with (CH₃COOH)₂ Zn·2H₂O and produces the nitro group. The peaks located at 1119.771 cm⁻¹ and 1004.77 cm⁻¹ are the stretching vibration peaks of C—O group. It shows that there exists some acetates that don't participate in the reaction.

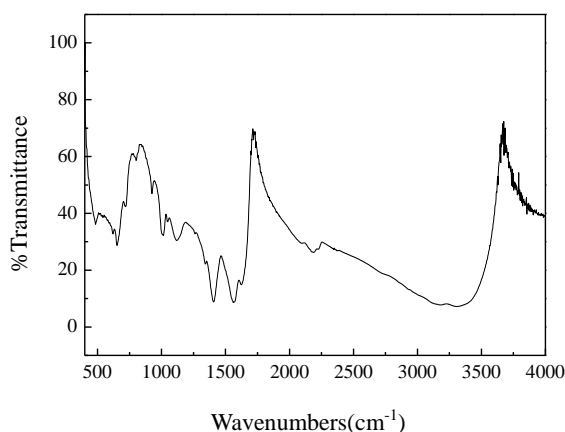


Fig.6 The infrared absorption spectrum of ZnS:Mg²⁺ quantum dots

4. Conclusion

Pure ZnS and ZnS:Mg²⁺ quantum dots are prepared successfully by aqueous phase method. The XRD patterns show that they belong to cubic sphalerite structures. The TEM images show that these two samples are approximate to spheres. The average particle size is about 4nm. They distribute uniformly and have adhesion phenomenon. From fluorescence spectrum, we analyze that ZnS:Mg²⁺ quantum dots emit green light at 525nm, belonging to impurity level luminescence of Mg²⁺. By changing the doping concentration of Mg²⁺, the proportion of thiourea/ZnS and the pH value of mixed solution, we get that the best technological conditions are that the doping concentration is 1.5%, thiourea/ZnS is 1.5:1, pH value is 13. The infrared absorption spectrum shows that thiourea coats on the surface of ZnS and a part of it reacts with ZnS. Some acetates don't participate in the reaction.

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