2nd INTERNATIONAL CONFERENCE ON
RESEARCH IN SCIENCE AND TECHNOLOGY
Istanbul-Turkey 14 March 2016
RSTCONF
دومین کنفرانس بین المللی
پژوهش در علوم و تکنولوژی
ترکیه - استانبول ۲۴ اسفند ۱۳۹۴

Compare synthesis Different types of quantum particles CdSe/ZnS and investigation Specifications

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Abstract
The effect of additives on the *fluorescence spectra* of semiconductor nanoparticles was studied using CdSe/ZnS,particles of various sizes and composition. Based on the fluorescence quenching of quantum dots caused by material a simple, sensitive and rapid method was developed. In the end satisfactory results were obtained. The different synthesis methods was also discussed.
Keywords: synthesis, Quantum Dot, Nanoparticles CdSe/ZnS

Introduction

The use of quantum dots (QDs) for the development of sensors is one of the most developingfields of nanotechnology so far Their fluorescence efficiency is sensitive to different compounds on their surface. (Gema et al, 2015).Luminescent semiconductor nanoparticles, commonly referredto as‘quantum dots’ (QD), have had a profound impact on research in biological sensing, medical diagnostics and therapeutics The focus has evolved from QDs as passive sensing or imagingagents to exploration of their use as therapeutic agents in the treatment of disease, or as multifunctional platforms capable of simultaneous diagnostic and therapeutic modalities (theranostics)(Aravind et al, 2013). Quantum confinement effects are responsible for such remarkable properties, which depend on their size and composition Such effects offer the analyst high fluorescent quantum yields, narrow and symmetric size tuneable emission spectra, high resistance to photobleaching and long fluorescence lifetimes; features which can be highly useful for analytical purposes(Gema et al, 2013, Jie et al, 2014).

The synthesis of QDs can be divided into two categories: organic phase high temperature decomposition and aqueous phase synthesis. The organic phase high temperature synthesis can get nanoparticles with wide wavelengths, evenly dispersed, narrow particl size and high fluorescent intensity but poor water-soluble and serious flicker . The aqueous phase synthesis has been a hotspot for the obtained water-soluble QDs can be directly applied in thebiological field. Compared with the organic phase high temperature synthesis the fluorescence intensity of aqueous phase synthesis QDs is lower, but they have the obvious advantages of simple operation, controllable surface charge, stronger anti photobleaching ability, better optical properties and others. And along with the synthesis methods improved, the fluorescence intensity of aqueous phase synthesis QDs is enhanced greatly(Jianqiu et al, 2015, Jing, 2015).

Recently, fluorescence resonance energy transfer (FRET) has been widely implemented in biosensors(Hong and Jong2015).Fluorescence spectroscopy is a type of electromagnetic spectroscopy which analyzes fluorescence from a sample. It involves using a beam of light, usually ultraviolet light thatmexcites the electrons in molecules of certain compounds and causes them to emit light; typically, but not necessarily,visible light . A complementary technique is absorption spectroscopy.

The core – shell materials consist of a core structural domain covered by a shell do-main. The core and shell may be composed of variety of materials including polymers, inor-ganic solids, and metals; they have properties which may be different from the core or the shell materials(H. I. Murad et al,2013)

Synthesis of CdSe/ZnS

1. Preparation of colloidal CdSe nanoparticles

The cadmium selenide CdSe nanoparticles were preparedas a colloidal by chemical reaction of sodium selenosulfide Na_2SeSO_3 of 20 mM and cadmium chloride $CdCl_2$with gelatin of 40 mM solutions at 1:2 mole ratio. The Na_2SeSO_3solution was prepared by dissolving 0.504 g of Na_2SO_3 in 100 ml distilled water, followed by the addition of 0.158 g selenium Se powder to the Na_2SO_3 solution. After that, the mixture has been heated to 80˚C and maintained at this temperature for three hours. Finally, the Na_2SeSO_3solution was sealed and saved in the dark. The $CdCl_2$with gelatin solution was prepared by dissolving 0.438 g of $CdCl_2$in 50 ml distilled water, followed by addition 0.1 g of gelatin.

The mixture was then heated to 50˚C for 5 minutes. Ammonium hydroxide was used to adjust the pH of the solution to the required 8.4 pH level. The two solutions ($CdCl_2$with gelatin and Na_2SeSO_3) were mixed in a three-neck flask and left on magnetic stirrer at 25˚C with continuous flowing of argon gas for 30 minutes, until the formation of CdSe nanostructures.

2. Preparation of colloidal ZnS nanoparticles

The zinc sulfide ZnS nanoparticle were prepared by mixing two chemical solutions of 0.1 M.The first one, was prepared by dissolving 0.27 g of zinc chloride powder $ZnCl_2$in 20 ml distilled water. While the second solution was obtained by dissolving 0.156 g from sodium sulfide powder Na_2S in 20 ml distilled water. The two solutions were mixed in a three-neck flask and were lefton magnetic stirrer at roomtemperature with continuous flowing of argon gas for about one hour until the ZnS nanoparticles were formed.

3. Preparation of CdSe/ZnS core-shell nanoparticles

The CdSe/ZnS core-shell nanostructures were prepared by chemical reaction of 12 ml CdCl2with gelatin solution and 6 ml Na2SeSO3solution at 2:1 molar ratio in three- neck flask, followed by the addition of 20 ml of ZnS solution. The solutions mixed in the three-neck flask were left on magnetic stirrer at 50 ˚C temperature with continuous flowing of argon gas for about one hour until the CdSe/ZnS core-shell nanostructures were formed and then, isopropanol was added followed by centrifugation.(Abdulla et al,2012)

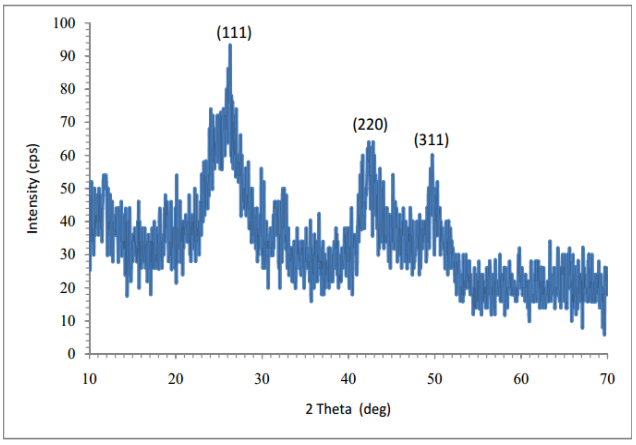

Figure 1. The XRD pattern of CdSe/ZnS core-shell nanoparticles

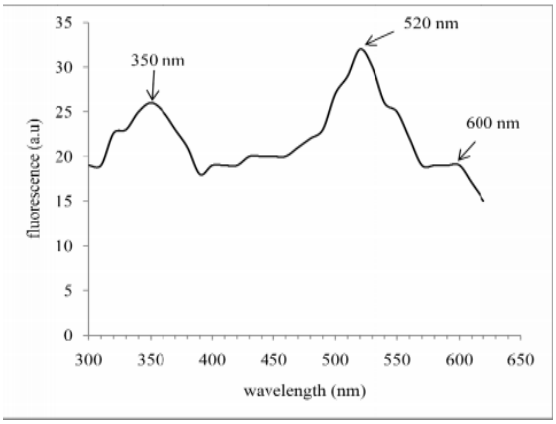

Figure 2.Photoluminescence emission spectrum of CdSe/ZnS core-shell solution(λ_{ex}=280nm)

Figure 3. A photograph of white light generation by GaN-UV LED CdSe/ZnS core-shell solution

Synthesis of CdSe/ZnS

1. Synthesis of CdSe NPs

CdSe nanoparticles were prepared by the reverse micelles technique. Three solutions with water to surfactant ratio (W_0)of 10, 20, and 30 were prepared. A 0.1 M solution of AOT was prepared in Isooctane. $CdCl_2$ (0.1) M solution was prepared in double distilled water. Two separate reverse micelle solutions were prepared using $CdCl_2$ and Na_2SeSO_3solutions. Under quick stirring, $CdCl_2$ solution (according toW_0 ratio) was added to one part of the reverse micelle, Na_2SeSO_3solution was added to another part of the AOT solution. Then the reverse micelle containing cadmium ion was slowly added to selenium reverse micelle solution. The CdSe ratio was kept as 1:1 in the present work. The CdSe yellow-orange color was observed after some time, depending on theW0content. The CdSe nanoparticle synthesis in the water pool of the reverse micelle can be written as follows.

2.Capping with ZnS

For ZnS capping, 0.1 M zinc chloride and Na_2S solutions were prepared in distilled water. Separate reverse micelles were prepared using zinc chloride and Na_2S in AOT/isooctane solution. The water content for the ZnS over layer preparation was kept similar to that in which the CdSe NPs were

synthesized. To CdSe NP solution 5 ml ZnS reverse micelle was added. Then 5 ml of Na_2S reverse micelle was added by drop wise to the above starting CdSe micelle solution under stirring. S^{2-} ions could react with Zn^{2+} ions on the surface of the CdSe core-forming a layer of ZnS on the CdSe cores.(Radheshyam et al,2009)

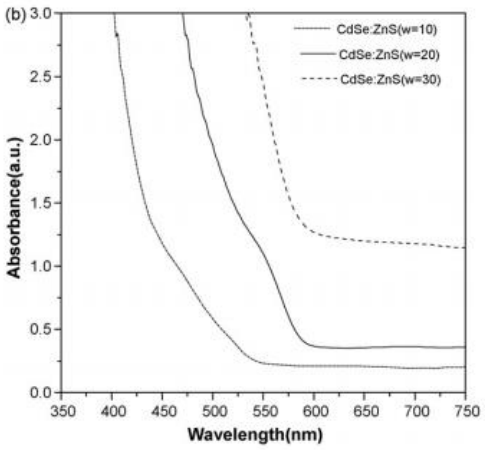

Figure 4.UV–vis spectra for CdSe/ZnS NPs

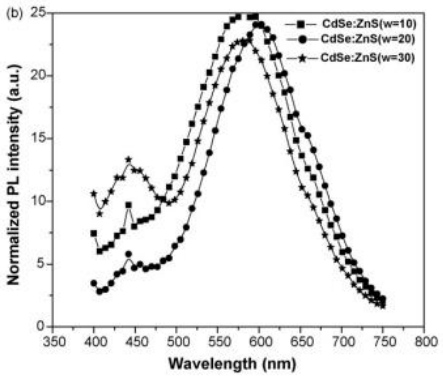

Figure 5.Photoluminescence spectra for ZnS capped CdSe NPs.

Synthesis of CdSe/ZnS

CdSe nanoparticles (ca. 40 mg) were dispersed in chloroform (5 cm^3) and added to a degassed mixture of hexadecylamine (3 g) and trioctylphosphine oxide (5 g) at 190°C. The mixture was placed under vacuum in order to remove the chloroform and the flask was back filled with argon and a stock solution of zinc stearate and sulfur in 1:1 trioctylphosphine/ toluene (10 cm^3) was added dropwise over 1 h by cannula. After this addition, the resulting solution was allowed to stir at 190°C for 75 min. Once the solution had cooled to room temperature, the particles were isolated by dissolution in chloroform (25 cm^3) followed by precipitation using an equal volume of methanol. Typical yield 210 mg. The stock solution used above was prepared by adding zinc stearate (1 mmol, 632 mg) and sulfur (1 mmol, 32 mg) to a Schlenk tube and degassing. Trioctylphosphine (5 cm^3) was added to the solid under argon and the mixture was sonicated.After dissolution of the sulfur, toluene (5 cm^3) was added and heated gently to form an optically clear solution.(Joseph et al, 2005)

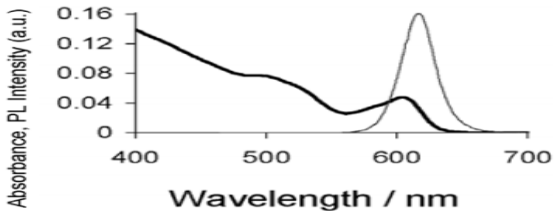

Fig. 6. UV/vis and fluorescence spectra of 4.3 nm core CdSe/ZnS particles

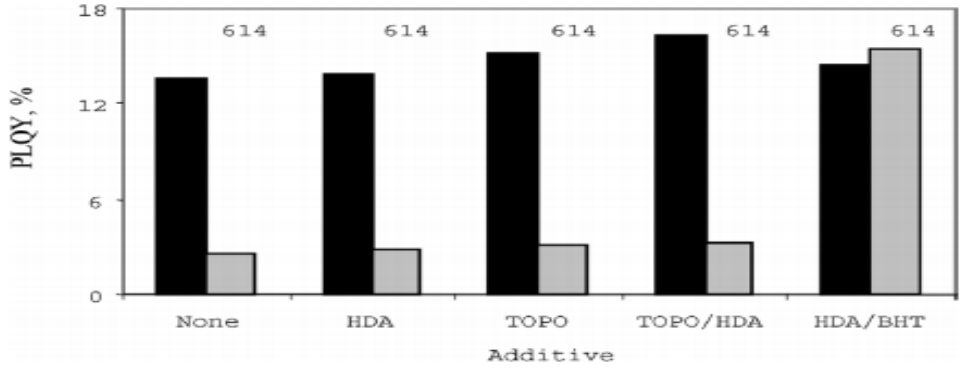

Chart 1. PLQY values for 4.3 nm CdSe core ZnS coated particles in chloroform. The numerical values above each bar are the λ_{max}(nm) of thefluorescence spectra after 1 week of exposure to light/air. The value of λ_{max} immediately after sample preparation was 616 nm.

Conclusion

In conclusion, we have synthesized a series of paramagnetic and luminescent nanoparticles with high quantum yield and relaxivity and simple, rapid and sensitive method for material analysis has been established based on the fluorescence intensity quenching of CdSe/ZnS QDs.

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