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Synthesis of zinc sulfide semiconductor nanoparticles by coprecipitation method for biological diagnostics

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Zinc Sulfide nanoparticles of the cubic zinc blende structure with the average crystallite size of about 3-5 nm were synthesized using a coprecipitation method and were stabilized with Sodium Tripolyphosphate. Then the room-temperature photoluminescence (PL) of zinc sulfide (ZnS) nanoparticles were investigated. Surface modification was carried out by linking Thioglycolic acid to the nanoparticles' surface in order to enable linking nanoparticles up with biological components such as Biotin. Luminescence spectra observations of nanoparticles illustrated a blue emission band in the range of 370-430 nm as a result of Copper dopant. Further more, Spectroscopy analysis of resulted complex proved that the emission intensity of nanoparticles decreases due to the increasing of Biotin amount. Therefore, the amount of biological material can easily be detected through measuring optical properties of these biological fluorescent markers.

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1. Introduction

The emission tunability of semiconductor nanocrystals renders them useful as chromophores for a wide range of applications such as biological fluorescent markers, light-emitting diodes, cell tracking, cell labeling and in vivo imaging [1-3]. Semiconductor quantum dots can be excited by a broader range of wavelengths and emit a narrower wavelength band[4]. Many of the developments in colloidal quantum dots are based on their size which is the size of a typical protein and therefore make it possible to introduce quantum dots into cells. The early experiments of using colloidal quantum dots for biological labeling were reported by Alivisatos et al. [1] and Nie et al. [5] in 1998. Nowadays semiconductor quantum dots have been studied as the labeling agent of the biological materials, cells and tissues[4].

Quantum dots have discrete electron layers and their band gaps can be easily tuned through size variation. Nanosized semiconductor crystallites could change optical properties which are different from bulk materials. This is the so-called quantum confinement that is observed as a blue-shift in absorption spectra with a decrease of particle size [6,7]. As the size is reduced to approach the exciton Bohr radius, there are some drastic changes in the electronic structure and physical properties, for example, a shift to higher energy [8-11].

These quantum effects begin to appear when materials become smaller than the Bohr exciton radius, generally around 100 nm or less in diameter. The optical and catalytic properties of such compounds are dominated by quantum confinement and surface effects. Changes to smaller particle size blue shift the absorbance spectrum of the molecule and with a corresponding change in the bandgap energy to higher energy [12].

A prerequisite in utilizing colloidal nanoparticles is that they remain stable in colloidal suspension. Stabilization mechanism of nanoparticles can be categorized as *a) electrostatic stabilization:* involving the creation of a double layer of adsorbed ions over the nanoparticles resulting in a coulombic repulsion between approaching nanoparticles; or b) *Steric hindrance:* achieved by adsorption of polymer molecules over the nanoparticles.

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Traditional methods for detecting biological compounds in vivo and in vitro rely on the use of radioactive markers. These labels are effective because of the high degree of sensitivity for the detection of radioactivity. However, many basic difficulties exist with the use of radioisotopes. Such problems include the need for specially trained personnel, general safety issues when working with radioactivity, inherently short half-lives with many commonly used isotopes, and disposal problems due to full landfills and governmental regulations. As a result, current efforts have shifted to utilizing non-radioactive methods of detecting biological compounds. These meth-

ods often consist of the use of fluorescent molecules as tags or the use of chemiluminescence as a method of detection.

In recent years, many research groups have studied association of semiconductor nanocrystals (quantum dots) with a reagent or molecule such that the composition can detect the presence and amounts of biological compounds. Without limitation, these reagents or molecules include any molecule or molecular complex that can interact with a biological target, molecules or molecular complexes that can associate with biological targets to detect biological processes, or reactions, and molecules or molecular complexes that can alter biological molecules or processes [10-14].

In this research, zinc sulfide nanoparticles were synthesized by coprecipitation method and were stabilized by sodium tripolyphosphate. Then, the phosphorescent nanocrystals were linked to an affinity molecule (Thioglycolic acid) to form organo-phosphorescent nanocrystals capable of bonding to biological targets like biotin. . The amount of biological material can be detected through measuring optical properties of nanoparticles.

2. Experimental

All the materials used in this synthesis were purchased from Merck and used as received. The Zns:Cu nanoparticles were synthesized by precipitation from a homogeneous aqueous solution Containing reagents. All the steps of the synthesis were performed at room temperature. $Zn(NO_3).4H_2O$ was added to 10mL of deionized water. Then aqueous solutions of sodium tripolyphosphate and $Cu(SO_4).5H_2O$ were added to the reaction medium and mixed for 30 minutes and pH was adjusted to 10.3 with 0.3 M NaOH. Na_2S was dissolved in deionized water and added dropwise to the reaction medium. Constant stirring was continued for 90 minutes yielding a colloidal white solution. After performing required analysis such as X-ray powder diffraction, Scanning Electron Microscopy, Transmission Electron Microscopy and ..., Thioglycolic acid was added to the resulted colloidal solution to enable nanoparticles to link to Biotin.

X-ray powder diffraction (XRD) patterns were detected by using a Philips Expertpro X-ray diffractometer with $Cu_{k\alpha}$ irradiation (λ = 1.54056 Å). Luminescence spectra were collected with a Perkin-Elmer LS-5 UV-visible spectrophotometer.

3. Results and disscusion

XRD analysis showed that these nanoparticles exhibit zinc blende crystal structure (Fig. 1). No significant characteristic peaks of impurity phases (such as CuS and CuO) have been observed. The diffraction spectrum of nanocrystals has three similar characteristic peaks index as the (111),(220) and (311) planes of cubic zinc blende phase. The average size of crystallites estimated by the Scherrer formula was 3-5 nm. From the XRD patterns, the broadening of the diffraction peaks of the nanoparticles is obvious, which is due to the nanosized materials.

Fig. 2 displays the excitation spectrum of Zinc Sulfide nanoparticles. The excitation wavelength of these nanoparticles is in a narrow range; therefore, this allows the simultaneous excitation of all populations of semiconductor nanocrystals in a system having distinct emission spectra with a single light source, with excitation wavelength about 263 nm.

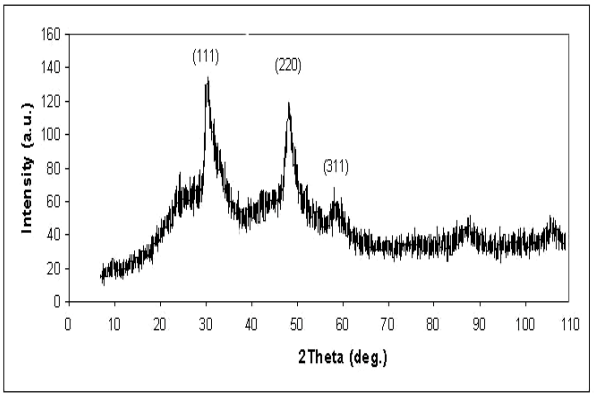

Fig. 1. XRD pattern of ZnS nanoparticles.

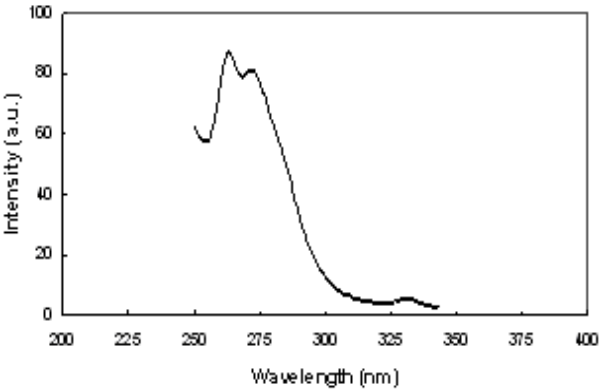

Fig. 2. Excitation spectrum of synthesized Zinc Sulfide nanoparticle.

The room temperature luminescence spectrum of the ZnS:Cu nanoparticles is shown in Fig. 3. A 450-nm-centered emission is observed in all the samples, which is defect related and assigned to SA luminescence of ZnS nanocrystallite. The maximum emission of the undoped ZnS nanoparticles is at 450 nm, but different emission intensities have been observed, when these nanoparticles are doped with Cu, due to the amount of dopant. The luminescence intensity of Cu-doped samples is decreased as the Cu-doped ratio was increased above the 0.5 molar percent. The spectrum is narrow and symmetric.

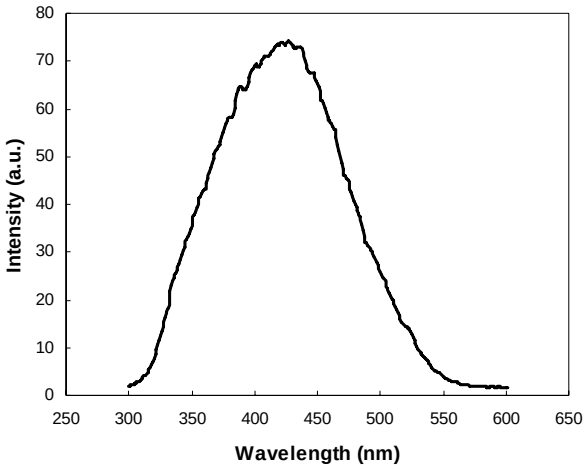

Fig. 3. Room temperature luminescence spectrum of the ZnS nanoparticles.

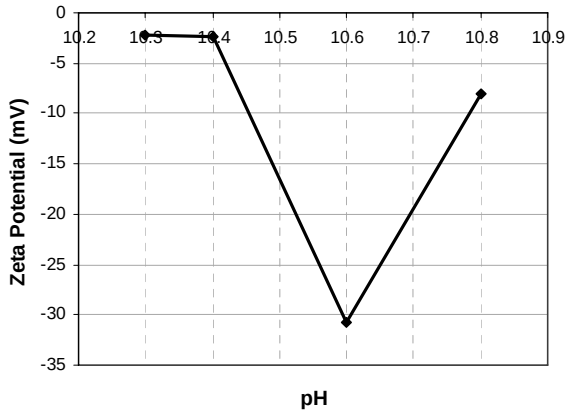

Fig. 4. Zeta potential of ZnS nanoparticles with different pH.

Fig. 4 illustrates the effect of pH on the zeta potential of the colloidal solutions containing synthesized nanoparticles. It's obvious that the solution with pH equal to 10.6 has the least zeta potential (-30.7) and consequently the nanoparticles have the maximum stability in the suspension. As this electric potential approaches zero, particles tend to aggregate. Zeta potential is an important and useful indicator of this charge which can be used to predict and control the stability of colloidal suspensions. The greater the zeta potential the more likely the suspension is to be stable because the charged particles repel one another and thus overcome the natural tendency to aggregate. The measurement of zeta potential is often the key to understanding dispersion and aggregation processes. Other samples have zeta potentials in the range of -8.1 to -30.7 which is due to the pH variation.

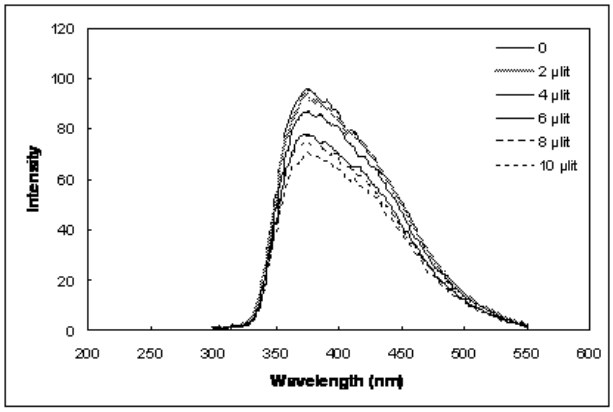

Fig. 5. Effect of adding different concentrations of Biotin as a biological target material to the colloidal solution containing of ZnS: Cu nanoparticles.

Studying optical properties of resulted complex when it was linked to Biotin (Fig. 5) revealed that the highest luminescence intensity is for the solution without any Biotin and therefore as the amount of Biotin increases, emission intensity of nanoparticles decreases and consequently by adding more Biotin, decreasing rate of emission intensity will continue**.**

4. Conclusions

Optimum condition and mechanisms required to synthesize monodisperse nanoparticle of ZnS:Cu were explored. Synthesis of ZnS nanoparticles doped with manganese was successfully carried out. X-ray Diffraction analysis showed that samples had cubic zinc blend structure with the average size of crystallites about 3-5 nm. Photoluminescence spectra of copper doped ZnS nanoparticles showed a single blue emission band in the range of 370-430 nm .Spectroscopy analysis of resulted complex proved that the emission intensity of nanoparticles decreases due to the increasing of Biotin amount. Therefore, the amount of biological material can easily be detected through measuring optical properties of these biological fluorescent markers. The resulted complex by way of example can detect the presence or amounts of a biological moiety (e.g. Biotin). Because detection of biological compounds is most preferably carried out in aqueous media, a preferred embodiment of the present research, utilizes nanoparticles that are solubilized in water.

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