Synthesis of Zinc Sulphide Nanostructures by Co-precipitation: Effects of Doping on Electro-optical Properties

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Abstract

In this article, we report the synthesis, optical and electrical properties of pure ZnS and Cu-doped ZnS nanoparticles. The ultraviolet-visible spectroscopy and steady-state photoluminescence suggested that the band gap of the pure ZnS occurs at ~3.75 eV, while the Cu-doping introduce a significant red shift in the absorption and emission spectra. The photoluminescence spectrum exhibited much wider emission with an additional feature peaking at ~3.51 eV. This feature in the photoluminescence spectrum is attributed to the existence of states introduced by Cu doping. The X-ray diffraction measurements revealed that the nanoparticles are grown in zinc blende crystal structure phase and the doping has not altered the crystal structure of the nanoparticles. Furthermore, we have performed the conductivity measurements of ZnS nanoparticles using four probe resistivity method, the Cu-doped ZnS nanoparticles exhibit higher conductivity as compared to the un-doped counter partners under the same conditions of UV irradiation. These observations are consistent with the red shift in the UV-visible and photoluminescence spectra, because doping with Cu decreases the band gap, which as a result helps to increase the photoconductivity of the nanoparticles under same UV irradiation.

Introduction

Semiconducting materials play a vital role in current electronic technology. In the last few decades, the earlier transmitting and receiving equipment which relied on vacuum tubes, have almost been replaced by the modern semiconductors, which include solid state devices such as transistors, diodes and integrated circuits. Various properties of semiconducting materials have been studied, but electrical and optical properties have been studied very extensively in the past decades [1-4]. The behaviour of the nanostructured semiconducting materials is very different from the bulk semiconductor materials. The nanostructured semiconducting materials have optical and electrical properties intermediate between macrorystalline solids and molecular entities. Recently it has fuelled a great deal of interest in the field of synthesis of nanostructured materials using wet chemical methods. The nanostructured semiconductor materials offer unique properties owing to large number of surface atoms and the three dimensional confinement of electrons in the crystal structure [5]. The electrical and optical properties of nanostructured materials depend on band gap values. The band structure of these materials changes with size. As the particle size is decreased from the bulk to the nano regime the band gap is increased and the band edges split into discreet energy levels, known as quantum-confinement effects [6]. The key requirement for practical applications of these materials is to control the electrical and optical properties. These properties can be controlled by controlling the size of the nanostructures and by the number of charge carriers. The number of charge carriers can be controlled by doping. Doped semiconductors contain impurities of foreign atoms which are incorporated into the host crystal intentionally or unintentionally [7]. So in order to utilize the nanostructured semiconductors as building blocks of functional nano-devices, it is very important to synthesize the nanoparticles having diverse physical properties. The diversity in the properties can be achieved via appropriate doping. Transition metal ions doped nanostructured materials are the most popular candidates from research point of view. Doped nanocrystals of semiconductor can yield high luminescence [8] and form a new class of luminescent materials, with large number of applications for instance, in displays, sensors and lasers etc. [9].

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Zinc sulfide (ZnS) has traditionally shown remarkable
fundamental properties versatility and a promise for novel diverse applications, including light-emitting diodes (LEDs) [10], electroluminescence [11], flat panel displays [12], sensors [13], lasers [14], and bio-devices [15]. The photoluminescence mechanism of ZnS nanocrystals doped with other metal ions is very complex. Small particles have higher surface to volume ratio and hence have more accessible carriers for photoluminescence [16]. The ZnS is an important II-VI chalcogenide with potential applications in electronic and optoelectronics because of its wide direct band gap, 3.77 eV for the wurtzite structure [16] and 3.72 eV for the zinc blende structure [17]. ZnS has high resistance to photo-chemical degradation. It can absorb the fraction of the solar radiation which is carcinogenic in nature, and it is relatively of low cost and non-toxic. It can be crystallized into two allotropic forms, a cubic form with zinc-blende (ZB) crystal structure and a hexagonal form with wurtzite (WZ) crystal structure. The former is stable at low temperature, while the latter is the high temperature polymorph which can be formed at the temperature of around 1296 K [18]. However, the nano-structures of ZnS have not been investigated in much detail.

Over the past few years, considerable efforts have been placed on the synthesis of ZnS nanostructures. The reduced dimensions of nano-structured materials enable one to reduce the size of electronic circuitry. They are expected to have higher quantum efficiencies due to increased oscillator strengths as a result of quantum confinement effects. A threshold for the occurrence of quantum effects is given by the value of Bohr radius of exciton in the bulk material [14]. As a representative of wide band gap II-VI semiconductor nanocrystals, ZnS has been synthesized by different methods. ZnS has a band gap of 3.66 eV at the temperature of 300 K. This corresponds to ultraviolet (UV) radiation for optical inter-band transitions. It is an important inorganic binary semiconductor material for a variety of applications including photoconductors, solar cells, field effect transistors, sensors, transducers and optical coatings [15-18]. It has been gaining importance in research community because of its diverse applications.

In this work we report the synthesis and the results of optical and electrical measurements of ZnS nanoparticles. The synthesis and Cu-doping of ZnS have been achieved at low temperature at 60°C. The doping give a red shift in the photoluminescence (PL) spectrum, which indicates the existence of states below the band gap edge of the pure ZnS. This suggests that the doping can help to tune the band gap from near UV to visible region of the ZnS nano-structures and the implications of the band gap tuning have been discussed relevant to electrical and optical properties. By tuning the band gap a diversity in optical and electrical properties can be achieved and make these nano-structured materials suitable for many practical applications.

**Experimental**

Zinc sulphide nanoparticles both un-doped and doped were synthesized by wet chemical or co-precipitation method. In this reaction we used deionized water as reaction medium. In a typical experiment 0.1M solutions of zinc acetate di-hydrate 

$$\text{Zn(CH}_3\text{COO)}_2\cdot2\text{H}_2\text{O}$$

was prepared in deionized water at room temperature. An equimolar solution of sodium sulphide nona-hydrate Na$_2$S.9H2O was prepared in the same reaction medium. Zinc acetate was allowed to dissolve completely in deionized water under vigorous magnetic stirring, until a clear homogeneous solution was formed. After this the solution was stirred for 30 minutes. Then equimolar solution of sodium sulphide was added drop-wise into the metal precursor solution. When sodium sulphide solution was added a milky mixture was formed indicating the formation of zinc sulphide nanoparticles. The resulting mixture was stirred for two hours. The white precipitates of zinc sulphide were collected by centrifugation and washed with distilled water and ethanol for three times. The washed precipitates were collected and dried at 80 °C. In order to dope the ZnS nanoparticles the metal precursor solution was stirred with 10 % (10 weight percent of Cu(CH$_3$COO)$_2$) corresponds to ~7.0 × 10$^{22}$ atoms of Cu available for doping) copper acetate for one hour and then sodium sulphide solution was added drop wise until the precipitates were formed. The resulting precipitates were centrifuged and washed with distilled water and ethanol three times, and were dried in oven at 80°C.

The scanning electron microscope (SEM) images were obtained by using SEM (LEO 440i) attached to Energy Dispersive X-rays system (EDX). The absorption spectra of these samples were collected by using UV-vis (Shimadzu 1601) spectrophotometer and the photoluminescence spectra of ZnS and Cu-doped ZnS nanoparticles were recorded with Fluorescence Spectrophotometer (Hitachi F-7000, 2133-007) by being excited at 275 nm. The X-ray diffraction (XRD) spectra of ZnS and Cu-doped nanostructures were collected by using the instrument (Orion The Netherlands, 3040/60, X’Pert Pro) equipped with copper Kα radiation source in the 20 range of 10-60°. The Fourier transformed infra-red (FTIR) spectra of doped and un-doped ZnS nanoparticles were measured by Thermo Scientific Nicolet-6700 FT-IR spectrometer. The electrical properties of ZnS nanostructures were assessed by Keithley's 2400 series general purpose source meter. To measure the resistivity, the powder samples of ZnS were converted to pellets by using hydraulic press by applying pressure of ca. 2 tons. The pellet of each sample was amounted on a glass slab and four wires were connected to the instrument, in order to measure the resistivity of the samples.

**Results and Discussion**

The morphologies of pure and Cu-doped ZnS nanoparticles were analyzed by SEM and are depicted in figure 1(a) and 1(b), respectively. From the SEM images of ZnS nanostructures it can be seen that both the un-doped and Cu-doped nanoparticle have been synthesized in spherical shapes, they are agglomerated...
and appeared in the form of nanocrystallites. Within the given resolution of SEM images, it indicates that the doping has not changed the morphology of the ZnS nanostructures, figure 1(a) and 1(b).

Absorption spectra were measured by completely dispersing the synthesized ZnS nanoparticles in ethanol. The room temperature absorption spectra of un-doped and Cu-doped ZnS nanoparticles are shown in figure 2. The absorption edge seems to appear at approximately 320 nm.

In order to determine the band gap of doped and un-doped ZnS nanoparticles absorbance square ($A^2$) versus energy (eV) was plotted, and by extrapolating the steepest part of the curve band gap was estimated and is shown in figure 3. This figure suggests that the Cu-doped ZnS nanoparticles showed a red shift as compared to the un-doped ZnS nanoparticles, indicating doping has reduced the optical band gap of ZnS nanoparticles. The band gap of un-doped and doped ZnS nanoparticles occurred at 3.77 eV and 3.0 eV. The red shift in the band gap is approximately 770 meV. This reduction in band gap is quite prominent which shows that the doping has altered the band gap of ZnS nanoparticles from near UV to visible region.

The room temperature PL is presented in figure 4. The PL spectrum shows a maximum at ca. 327 nm (3.79 eV) indicating the band edge emission followed by a red tail spreading approximately 500 nm. The origin of red tail can be attributed to zinc and sulphur vacancies and due to the sulphur bonds dangling at the interface of ZnS grains [19]. The observation of single emission peak followed by small peaks occurring at red region is also in consistent with the other reports [20-22].

While, in the case of Cu-doped ZnS nanoparticles an additional feature is observed peaking at 360 nm (3.44 eV) The existence of additional feature can be attributed to the emission from trap states which are introduced by Cu doping. These trap states also quench the PL of un-doped ZnS nanoparticles as demonstrated by dashed

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**Figure 1.** SEM images of (a) pure ZnS nanocrystallites and (b) Cu-doped ZnS nanocrystallites.

**Figure 2:** UV-visible absorption spectra of un-doped and Cu-doped ZnS nanoparticles.

**Figure 3:** Absorption square versus energy plot of pure and Cu-doped ZnS nanoparticles and band gap estimation.
Following excitation at 275 nm the electron from the valence band is excited into the conduction band leaving a hole in the valence band. The PL process occurs when the photoexcited electron from the conduction band recombines with the hole in the valence band. The occurrence of additional peak with slight less intensity is due to defects, which are introduced by Cu⁺ ions doping. This emission peak might be due to the transitions from the conducting bands to the t² levels of excited Cu²⁺ ions (d⁹) introduced by dopant [19,23,24].

In order to develop understanding regarding the crystal structure of the nano-structures, XRD analysis was performed for un-doped and Cu-doped ZnS nanoparticles, which were synthesized at room temperature. XRD analysis can give information about the crystalline or amorphous nature of the material. The sharp peaks show the crystalline nature of material and a broad hump appears when material gets amorphous, or the broadening of the peak also occurs when the nano-structures get agglomerated. The broadening of the peak may also appear due to the strains produced by dopant or it may be due to the deformation of crystal structure. The XRD measurements results have been presented in figure 5.

The XRD pattern revealed the cubic zinc blende crystal structure of ZnS nanoparticles. Three prominent peaks corresponding to the lattice planes (111), (220), and (311) are present confirming that ZnS nanomaterials are existing in zinc blende crystal structure. In the XRD pattern of copper doped ZnS, same three peaks at the same positions are observed. The peak intensities of un-doped and Cu-doped slightly differ and this difference is might be due to the non-uniformity of the samples. The XRD patterns also rule out the existence of any impurity, for instance CuO and Cu₂S due to the presence of copper. The existence of ZnS nanoparticles in zinc blende crystal structure phase is also consistent with the previous report [25], in which the ZnS nanocrystals have been grown in specifically in wurtzite phase at low temperature, but due to very small differences in the zinc blende and wurtzite structure of ZnS the existence of ZnS in zinc blende phase could not be excluded.

The FT-IR spectra of un-doped and Cu-doped ZnS nanoparticles are recorded between 400 – 4000 cm⁻¹ and are presented in figure 6. The peaks appearing at 490, 615 and 1110 cm⁻¹ belong to Zn-S vibrations. However, in the case of Cu-doping the peaks intensities at aforementioned wavenumbers have been decreased, which is an indication of successful doping. The obtained peaks values are in good agreement with the previous reports [26]. The presence of peaks between 1150-1800 cm⁻¹ are may be due the sulphur-oxygen interaction and the adsorption of water molecules on the surface of the nanoparticles. The peak observed at 2365 cm⁻¹ is due to the C=O stretching modes because of the presence of atmospheric CO₂, which might adsorb on the
surface of the nanoparticles. The broad absorption peak occurring in the range of 2950 – 3490 cm⁻¹ is due the presence of –OH group, thus indicating the presence of water molecules on the surface of the ZnS nanoparticles [28].

The conductivity of the synthesized samples was measured by four probe resistivity method and the results of the measurements are presented in figure 7. As the synthesized ZnS nanoparticles absorb in the near UV region so the resistivity was measured for both dark and light conditions. The resistivity of samples was measured by Ohm’s law by calculating the gradient for each data set. The conductivity of the samples was calculated by reciprocating the resistivity. The conductivity in the presence of light is termed as photoconductivity. In order to assess the correct photoconductivity, the conductivity was also measured in the dark for both un-doped and Cu-doped ZnS nanoparticles.

There is approximately no difference in the measured dark conductivity. But when the pellets of the nanoparticles are exposed to UV light there is considerable increase in the conductivity. The increase in photoconductivity is due to the presence of photogenerated charge carriers (electron-hole pairs). This increase in the conductivity is slightly higher in Cu-doped ZnS (~8.32 × 10⁻⁸ S) nanoparticles as compared to the un-doped ZnS nanoparticles (~8.0 × 10⁻⁸ S). This indicates the presence of higher number of charge carriers in Cu-doped ZnS nanoparticles as compared to un-doped nanoparticles. This increase is also consistent with the existence of red shift in the band gap of Cu-doped ZnS nanoparticles. Owing to the reduced band gap of doped nanoparticles, shining near UV light on Cu-doped ZnS nanoparticles, the same photon flux generate higher number of electron-hole pairs as compared to un-doped nanoparticles, which results in increase in the photoconductivity. Thus, indicating an excellent agreement between optical studies (UV-Vis and PL measurements) and photo-conductivity measurements. The next step in future is to measure the PL lifetime of pure and Cu-doped ZnS nano-structures using the time correlated single photon counting technique. The life-time of the photo-generated charge carriers in these systems is relevant to the functioning of many ZnS nano-structured based devices.

Conclusions

We have reported the synthesis of ZnS nanoparticles by wet chemical method at low temperature of 60°C. The successful doping of the synthesized ZnS nanoparticles has been done using the aforementioned method. The band gap of pure ZnS and Cu-doped ZnS nanoparticles was found to occur at 3.77 eV and 3.0 eV, respectively. The doping introduced a red-shift of ~770 meV in the band gap of ZnS nanoparticles, thus shifting the band gap form near UV to the visible region. The occurrence of red shift in the PL spectrum of Cu-doped ZnS nanoparticles as compared to the un-doped nanoparticles confirmed the existence of emissive states below the band edge. These emissive states were introduced by Cu dopant. The XRD results confirmed that doping did not change the crystal structure and both the un-doped and Cu-doped ZnS nanoparticles existed in cubic zinc blende crystal structure. Furthermore, the photo-conductivity of the doped ZnS nanoparticles were higher at the same photon flux than the pure ZnS nanoparticles, this confirmed the presence of higher number of charge carriers in the case of doped ZnS nanoparticles. These findings were consistent with the red shift of band gap by Cu-doping. Owing to the red shift in the band gap near UV excitation injected the higher number of charge carriers at the same photon flux. This confirmed that Cu-doping introduced the surface states which help to increase the photo-conductivity of the ZnS nanoparticles.

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