Investigating the luminescent property of transition metal doped ZnS nanoparticles synthesised by co-precipitation method

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Abstract. The group II-IV nanoparticles have excellent semiconducting properties having a possibility of tuning it by changing the size, shape and precursors. This makes them an ideal candidate for their applications in the field of science and technology. Amongst several semiconductor nanoparticles, zinc sulphide (ZnS) nanoparticles are promising material because of chemical stability, low toxicity and better optical properties. Introducing transition metal impurities in ZnS nanoparticles further improves the physical properties like optical and magnetic. The synthesis and optical properties of transition metal doped ZnS nanoparticles with varying doping percentage is reported. The doping of ZnS with the transition metal with variable doping concentration improves the luminescence in comparison of pure ZnS. The photoluminescence spectrum has a single major peak at 780nm, and the intensity increases with the type and concentration of the impurity but at higher concentration the luminescence is quenching. This paper tries to give a comprehensive study of photoluminescence of ZnS nanoparticles doped with different transition metal with varying concentration.

1. Introduction

The semiconductor nanoparticles or quantum dots have created interest in recent years amongst the researchers due to their amazing physical properties which can be adjusted as per the requirements [1]. The ZnS in II-VI group is a wide band semiconductor with low toxicity, high stability and better photoluminescence with narrow emission spectra [2, 3]. The intensity of spectra can be adjusted by controlling the size and shape of the nanoparticles, semiconductor material and impurities introduced along with their concentration. Therefore they have become an alternative to the organic luminescent materials which have poor stability and tunability even in the field of biotechnology and medicine [4]. Therefore inorganic luminescent materials are ideal candidates not only in the field of biotechnology and medicine but also can be used for electroluminescent devices, photodiodes, photo-catalysis and dye degradation [5]. In recent years researchers are putting their best effort in the study of doped ZnS nanoparticles. The introduction of transition metal impurity improves optical properties to a great extent and magnetic properties to some extent.

Common transition metal preferred for doping are copper, iron, nickel, manganese and cobalt. The copper (Cu) doping in ZnS nanoparticles gives a photoluminescence peaks at 420nm and 510nm whose intensity almost got doubled upon the introduction of the impurity [6]. With the increase in the impurity percentage the luminescence shows quenching of the luminescence which has a maximum at 0.4% at wavelength of 445nm. Also the luminescence intensity and stability are improved by the addition of the surfactants [7]. With the doping of iron (Fe) ions photoluminescence intensity has a peak at 400nm with additional peak at 620nm. The photoluminescence peak has red shift if the doping percentage is
increased. Also, the peak intensity increases with increase of Fe concentration which peaks at 3%. [8]. But some of the reports have mentioned only the quenching of the photoluminescence [9]. Doping with nickel (Ni) enhances the photoluminescence intensity having a peak at 445nm for undoped, 472nm and 498nm for doped. With the increase in doping concentration the intensity increases which peaks at 0.5% and quenching thereafter [10]. In some of the studies, multiple peaks in the range of 400nm to 550nm have been reported [11]. The introduction of manganese (Mn) ion in the ZnS nanoparticle lattice enhances the photoluminescence intensity with red shift with a peak at 600nm [12]. In Mn doping, also, quenching was reported [13]. Another promising dopant from the transition group is cobalt (Co) which enhances the photoluminescence intensity which has a peak at 450nm with quenching of intensity [14].

It is an overall observation that the photoluminescence increases with the doping of the transition metals to some percentage and then shows quenching. All the above papers have reported blue-green emission for pure and doped ZnS nanoparticles. In some cases doping of the transition metal changes the emission wavelength, like, blue-green for copper and orange for Mn doping but in most of the cases the dopants only serve as the sensitising agent and do not change the emission wavelength.

In the above studies the samples were prepared by different chemical methods with varying precursors and physical conditions. A variety of surfactants in different concentration were used to avoid the agglomeration, controlling the crystal growth and improving the photoluminescence. This resulted in variety of particle size with different surface conditions, thus the studies undertaken were on different platforms and was not giving any information of actual change in the luminescent intensity. Also, we got a sharp peak for red emission for all the impurities and their different percentages. The present study is undertaken to select the best impurity and its concentration for the best photoluminescence.

2. Experimental

2.1. Synthesis

Pure and doped ZnS nanoparticles were synthesized by chemical co-precipitation method in ambient condition. All chemicals used were of analytical grade with no further purification and locally sourced. The pure ZnS nanoparticles were synthesized by the precipitation of 0.1M of zinc (0.8972gm of ZnSO₄H₂O in 50ml of deionized water) and 0.1M of sulphur (0.6604 gm of Na₂S in 50ml of deionized water). The zinc sulfate solution was taken in a beaker stirred continuously at 300rpm while the sodium sulfide solution was added drop wise with the help of a burette. The solutions were prepared in deionized water and the reaction was carried out at room temperature in ambient environment. The capping agent 1gm PVP was introduced in the reaction along with zinc sulfate to control the crystal growth and avoid agglomeration. A white precipitate appeared at the end of the reaction. The solution was continuously stirred at constant rpm for 2 hours. The precipitate formed in the reaction was collected and centrifuged at 5000rpm for 20 minutes. The ZnS nanoparticles got settled at the bottom of the centrifugation tube which was redispersed in deionized water with the help of sonication. For removing the impurities and unreacted chemicals, the process is repeated several times. Finally, the precipitate is collected and kept for drying in hot air oven for overnight. The dried sample was collected and crushed to fine powder in mortar-pestle.

The chemical reaction is as given below,

\[ \text{ZnSO}_4 + \text{Na}_2\text{S} \rightarrow \text{ZnS} + \text{Na}_2\text{SO}_4 \]

For doping, the salts of transition metals (1%, 2%, 5% and 10% of the molar value of MnSO₄ for Mn, NiCl₂ for Ni, FeCl₃ for Fe, CuSO₄ for Cu, CoCl₂ for Co) is added along with the zinc sulfate. Other steps of the synthesis remain unchanged.

2.2. Characterizations

Analysis of nanoparticles is done by using analytical techniques such as optical absorption, photoluminescence, XRD, EDAX and TEM.

The optical absorption spectra of nanoparticles were recorded by Labindia (UV-3000) UV–VIS spectrometer in the range of 200nm to 800nm. The Agilent (Cary Eclipse) was used to record the photoluminescence spectra. The XRD analysis was done by Rigaku (Ultima IV) operating at 40 KV-40 mA using CuKα radiation (λ = 1.5406 Å). The morphology of the synthesized nanoparticles was
examined by using transmission electron microscope (TEM) Technai (G² 20U Twin). The elemental analyses (EDAX) was carried out to confirm the formation and purity of the ZnS nanoparticles. For EDAX Bruker Quantax EDS attached with Sigma Zeiss HV field effect scanning electron microscope (FESEM) was used.

3. Results and discussion

3.1. Optical absorption studies

Figure 1 shows the absorption spectra for pure and transition metal doped (2%) ZnS nanoparticles. The spectra showed a sharp absorption edge with a shoulder at 320nm. The doping of the transition metals showed a minor blue shift in the absorption shoulder. But there is no noticeable shift due to the type of doping [15]. The band gap was calculated by using Tauc plot and is found to be 4.05eV for pure and 4.20 to 4.51eV for doped ZnS nanoparticles. The calculated band gap was higher than the bulk ZnS (3.68eV) which is by virtue of quantum confinement [16].

The radius was calculated by the equation.

\[
E(r) = E_{\text{bulk}} + \frac{\hbar^2}{8r^2} \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1.8e^2}{4\pi\varepsilon r}
\]

Where, \(E(r)\) is the band gap nanoparticles, \(E_{\text{bulk}}\) is the band gap of the bulk, \(m_e^*\) and \(m_h^*\) are the effective mass of electron and hole respectively. The third term is the Coulomb’s attractive force between electrons and holes which is negligible. The diameter of the nanoparticles calculated from above equation is approximately 3nm. A small decrease in the size of nanoparticles with the doping is observed which is due to quenching in the growth of nanoparticles [8].

3.2. Photoluminescence

In pure ZnS nanoparticle the photoluminescence is affected by the quantum confinement effect, thus the emission spectra of nanoparticles are size dependent, shifting to the blue with decrease in particle size. However, transition metal doped ZnS nanoparticles exhibited red-shift in the photoluminescent emission spectrum [17]. The photoluminescence measurement was performed at room temperature on pure and doped ZnS nanoparticles at an exciting wavelength of 390 nm which yields two peaks, one at 440nm and another centered at 780nm. The observed wavelengths are much higher than the reported values in most of the papers [18, 19] which may be due to the result of oxygen atoms trapped in the nanostructures. The oxygen atoms may have been trapped either due to atmospheric oxygen as the reaction was carried out in ambient condition or the capping agent PVP. The presence of oxygen atoms

![Figure 1. UV-VIS spectra of pure and doped (2%) ZnS nanoparticles](image-url)
was confirmed by the energy dispersive spectroscopy (EDS). These oxygen atoms form a trap level in the band gap of the ZnS nanoparticles, resulting new transition levels [20]. The figure 2 shows possible transition in ZnS nanoparticles. The emission at 440nm is due to the transition from the conduction band to the energy levels of interstitial sulphur (S\textsubscript{i}). The sharp red emission is due the transition between the energy level of trap oxygen (O\textsubscript{T}) to the energy levels of interstitial sulphur (S\textsubscript{i}).

With the increase of doping percentage the luminescence increases up to 1% doping and then decreases showing the quenching of the luminescence. Upon doping with transition metals it is observed that the peak wavelength value remains the same only the magnitude of the intensity changes. The emission peaks at different doping percentage for different doping materials. The quenching of luminescence has shown different behaviour for different doping percentage, the fall in the luminescence is slow in case of Mn doping and steep in the Cu doping. The higher doping concentration the dopant transition metal acts as electron trapping centres. This increases the non-radiative recombination reducing the radiative transitions [21-24]. The figure 3 shows the photoluminescence and relative photoluminescence of doped and undoped ZnS nanoparticles.

**Figure 2.** Possible transitions in ZnS nanoparticles
3.3. Structural and morphological studies

The XRD patterns of pure and doped ZnS nanoparticles have been shown in figure 4. The diffraction pattern has three well marked peaks for all samples at $2\theta = 28.6^\circ$, $47.8^\circ$, and $56.6^\circ$ for the miller planes (111), (220), and (311) respectively [25]. The XRD pattern matched with the cubic zinc blende structure, confirming the formation of the ZnS crystals. The addition of the impurity does not introduce any additional peaks confirming that the impurity atom is placed in the lattice structure of the ZnS crystal. The broadening of XRD peak is also observed which is due to nanosized particles [26]. Doping of the transition metal impurities resulted in a small decrease in the particles size of ZnS nanoparticles. The nanoparticle size quenching may be because of different ionic radii among ions of different elements. The ionic radii of are 0.74, 0.83, 0.69, 0.645, 0.73 and 0.65Å for Zn$^{2+}$, Mn$^{2+}$, Ni$^{2+}$, Fe$^{2+}$, Cu$^{2+}$ and Co$^{2+}$ ions, respectively. As the ionic radii of Zn$^{2+}$ are different than the ionic radii of the dopants this may be causing the nanoparticles to shrink in their size. The crystallite size was calculated by Debye Scherrer’s formula [27, 28],

$$d = \frac{k\lambda}{\beta \cos \theta}$$

Where $d$ is the diameter of nanocrystal, $k$ is the constant ($= 0.9$), $\lambda$ is wavelength of the X-ray ($= 1.54056$ Å), $\beta$ is the full width half maxima (FWHM), and $\theta$ is the Bragg angle. The average crystallite size was calculated to be in the range of 3nm.
Figure 4. XRD of pure and transition metal doped (2%) ZnS nanoparticles

The purity and the doping of the synthesised nanoparticles were confirmed by energy dispersive spectroscopy (EDS) spectra and the corresponding micrographs are shown in figure 5. The EDS spectrum of pure ZnS has the peaks corresponding to Zn and S which confirms the purity of the sample prepared. Whereas the transition metal doped ZnS nanoparticles have peaks corresponding to Zn, S and the doped transition metal confirming the doping of the synthesised nanoparticles [29, 30].

As per the calculations, the size of the synthesized nanoparticles are in the range of 3nm so FESEM has resolution limit and cannot be used for the morphological study. So, for the morphological studies transmission electron microscope (TEM) was used. The TEM images of pure ZnS nanoparticles, as shown in figure 6. It show that the nanoparticles are spherical in shape and monodispersed. The average size of the nanoparticles is well in agreement with the calculated value [31].
4. Conclusion
The pure and doped ZnS nanoparticles with an average size of 3nm were synthesized by chemical co-precipitation method at room temperature by using deionised water as solvent. The UV–visible absorption spectra showed a strong quantum confinement effect confirming the formation of nanoparticles. XRD showed cubic phase of all the synthesized samples without any changes in the crystal structure. The room temperature photoluminescence spectra of all the samples had peak positions at 440 and 780nm. The emission peak intensity increased with doping concentration initially and decreased beyond a critical value. The maximum intensity and the critical doping percentage were different for different doping materials. The highest luminescence was obtained for Mn (5%), which is sufficiently high as compared to other doping impurities. The sharp and single peak of photoluminescence makes it an ideal candidate for the imaging and tagging in biomedical application.

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