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Effect of UV radiation on the photoluminescent properties of Cu-doped ZnS nanoparticles

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In this paper, we report the changes in the photoluminescent properties of the Cu-doped ZnS nanoparticles upon prolonged UV irradiation in the atmospheric conditions. The chemical precipitation technique was employed to fabricate the Cu-doped ZnS nanoparticles (~ 2.5 nm) in an aqueous media, at room temperature, using polyvinyl pyridine as the surfactant. UV-Visible absorption studies have been used to calculate the band gap values of the fabricated ZnS:Cu nanoparticles. By Gaussian fitting, the PL spectrum was deconvoluted into three blue luminescence peaks (centered at 403.5 nm, 425 nm and 450 nm), attributed to the recombination of the defect states of ZnS and a blue-green peak (centered at 485nm). This blue-green luminescence may have originated from the recombination between the shallow donor level (sulfur vacancy) and the t_2 level of Cu^{2+}. An increase in the photoluminescence (PL) intensity, upon prolonged UV exposure to the ZnS:Cu nanoparticles, corresponds to an increase in the radiative transition probability, whereas no shift in the peak position was found.

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1. Introduction

The wide band gap ZnS (~3.6 eV) semiconductor has gained substantial interest in the research community due to its extensive range of applications from blue/green light-emitting diodes (LED) and electroluminescent devices (ELD) to optoelectric modulators [2]. Even though the research focusing the ZnS semiconductor as luminescent material goes back many decades, the renewed interests are fueled by the doping of a luminescent center (Mn^{2+}/ Cu^{2+} ions) into a nanosized ZnS matrix and investigating their optical properties which are remarkably different from the bulk. This can be attributed to the quantum size effects, due to which band gap can be tuned, enabling the tunability of the band-edge absorption and emission wavelengths [3].

Copper doped ZnS crystals are well known as classical luminophosphors as they have efficient phosphorescent properties and high photosensitivity [1]. Moreover, efforts have been made to study the optical properties of copper doped ZnS nanocrystals, not only because it is a widely luminescent materials, but also on account of the stronger interaction of copper ions with the host ZnS. The luminescent nanomaterials are particularly important as the properties of these materials are greatly influenced by various surface states arising out of the higher surface-to-volume ratio. The surface chemistry of the luminescent II-VI semiconductor nanocrystals has been extensively investigated to improve the luminescent characteristics such as quantum efficiency and photostability [3].

Numerous researchers [2, 6-9] have worked to synthesize and elaborate the mechanisms behind the changes in the optical properties of the Cu-doped ZnS nanoparticles. However, in this paper, we not only demonstrate the remarkable changes in the optical properties of the Cu-doped ZnS nanoparticles by varying the concentration of the dopant but also report the remarkable changes observed on their prolonged exposure to the UV radiations.

2. Experimental

(i) Synthesis

Doped zinc sulphide (ZnS) nanoparticles were synthesized by chemical precipitation from homogeneous solutions of zinc and copper salt compounds, with S^{2-} as precipitating anion, formed by decomposition of sodium sulphide. Homogeneous solutions of zinc acetate 0.5 M ($Zn(CH_3COO)_2.2H_2O$), copper sulphate ($CuSO_4.5H_2O$) and 0.5 M sodium sulphide were prepared in an aqueous media. The concentration of the dopant varied from 0.01 at. % to 10 at. %. The copper sulphate solution was slowly mixed with the zinc acetate solution at room temperature, which was followed by slowly adding the sodium sulphide solution and poly vinyl pyridine stirring constantly. Polyvinyl pyridine acts as a surfactant so as to control the size of the synthesized particles. Immediately after the injection of sodium sulphide solution a turbid fluid was obtained whose color varied from white to greenish white as the concentration of the dopant (copper) was increased. The stirring was further allowed for 20 minutes at room temperature. Then the precipitates, as collected, were twice washed with double distilled water and were dried in a vacuum oven at 60 °C.

(ii) Irradiation

All the samples were UV irradiated by a 40watt UV lamp at a wavelength of 255 nm for 24 hours at room temperature.

3. Characterization

X-ray diffraction (XRD) patterns of the doped ZnS nanoparticles were taken using a Seifert 3000P Diffractometer with Cu Kα radiation (λ=1.54178 Å). For transmission electron microscopy (TEM) study, a colloidal suspension of nanoparticles in ethanol was prepared by ultrasonic treatment, and, then, deposited on carbon-coated copper grid. UV-Visible absorption spectra were recorded by dispersing the nanoparticles in spectroscopic grade ethanol using a spectrophotometer (Hitachi U 3410). Photoluminescence (PL) measurements were carried out at room temperature with a luminescence spectrometer (Hitachi, FL 2500) using 325 nm as the excitation wavelength.

4. Results and discussion

The XRD pattern (Fig. 1) of the ZnS nanoparticles revealed the zinc-blende crystal structure. The three diffraction peaks respectively correspond to (111), (220) and (311) planes of the cubic crystalline ZnS. No characteristic peak, related to the dopant (such as CuS, CuO) has been observed in the XRD analysis. The average size of the ZnS:Cu crystallites, calculated using Debye-Scherrer formula [3], is 2-3 nm. The XRD patterns of the samples having various concentrations of the dopant as well as the respective samples, when exposed to UV radiation, are found to be identical with respect to the peak position and the peak broadening.

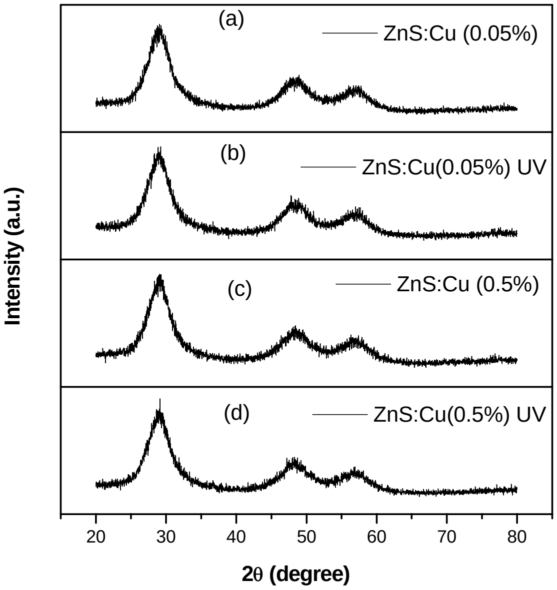

Fig. 1. XRD pattern of ZnS:Cu nanoparticles having various concentrations of Cu (a, b) 0.05 at. %, (c, d) 0.5 at. % ; (with and without UV irradiation).

Fig. 2(a) shows the transmission electron micrograph (TEM) of ZnS:Cu (0.5 at.%) nanoparticles. The diameters of most of these particles lie in the range 3-5 nm. These results are nearly in accordance with those of the X-ray diffraction analysis. The selected area diffraction pattern presented, in the inset of Fig. 2(b), shows the crystallinity of the fabricated nanoparticles. The dominant diffraction patterns in the micrograph are indexed as (111), (220) and (311) planes of the cubical ZnS.

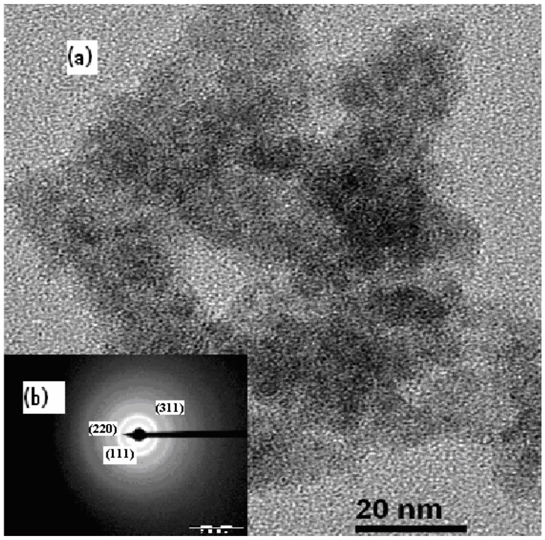

Fig. 2. TEM image of the ZnS:Cu (0.5%) nanoparticles aong with the SAED pattern in the inset.

The optical absorbance of all the synthesized ZnS:Cu samples has been measured and optical band gap (E_g), calculated. The absorption coefficient (α) is determined from the absorbance versus wavelength (λ) traces recorded for the ZnS: Cu nanoparticles. The optical band gap (E_g) in a semiconductor is determined by assuming the nature of transition (m) and plotting $(\alpha h\nu)^{1/m}$ versus hν, where m represents the nature of transition. Now, m may have different values respectively ½, 2, 3/2 or 3 for allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions [4]. For allowed direct transition $(\alpha h\nu)^2$ versus hν was plotted and the linear portion of it was extrapolated to $\alpha = 0$ value to obtain the corresponding band gap (E_g). The corresponding plots as a function of the copper concentration and on prolonged UV irradiation have been shown in Fig. 3. No significant shift, on UV-irradiation, in the absorption edge, has been observed. This can also be observed from the band gap values, as shown in Table 1, that there is no remarkable difference between the band gap values before and after UV- irradiation. There is slight increase in the band gap value of the ZnS:Cu nanoparticles (3.78 eV) from the bulk value (3.67 eV), which indicates the quantum size effects.

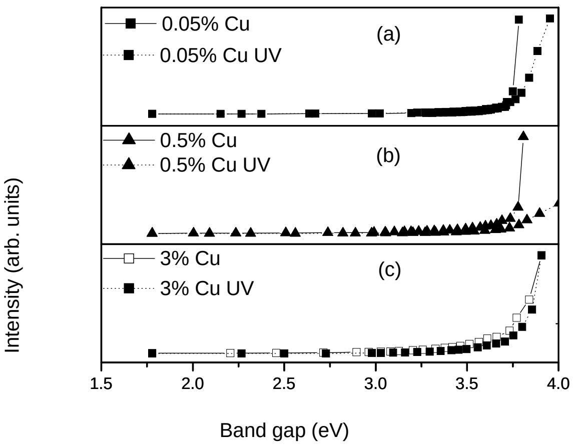

Fig. 3. UV-Visible absorption spectra of the ZnS:Cu nanoparticles with Cu concentrations (a) 0.05 % (b) 0.5 % (c) 3 %.

Table 1. Band gap values of the ZnS:Cu nanoparticles with and without UV-irradiation.

S. No.	Sample Name	Band Gap (eV)	
		Without UV-irradiation	With UV-irradiation
1.	ZnS:Cu (0.05%)	3.73	3.75
2.	ZnS:Cu (0.5%)	3.78	3.73
3.	ZnS:Cu (1%)	3.77	3.78

Fig. 4 shows the photoluminescence spectra of the ZnS:Cu nanoparticles upon 350 nm excitation. The spectra are broad and asymmetric; this shows the presence of more than one component. Gaussian curve fitting was applied to deconvolute the PL curves. The PL spectrum has been deconvoluted into three blue luminescence peaks centered at 403.5, 425 and 450 nm and a blue-green peak centered at 485 nm. The PL peaks at 403.5 nm and at 425 nm have been known due to the recombination of the electrons between the sulfur-vacancy–related donar and the valence band [5, 6]. As shown in Fig. 5, the peak positions of these blue luminescence peaks did not show a remarkable change as the Cu $^{2+}$ ion concentration was varied, which indicates that the energy level of sulfur vacancy remains almost constant relative to the valence band. The blue-green luminescence centered around 485 nm may have originated from the recombination of an electron from the shallow delocalized donor level (sulfur vacancy) to the t_2 level of Cu^{2+} [9].

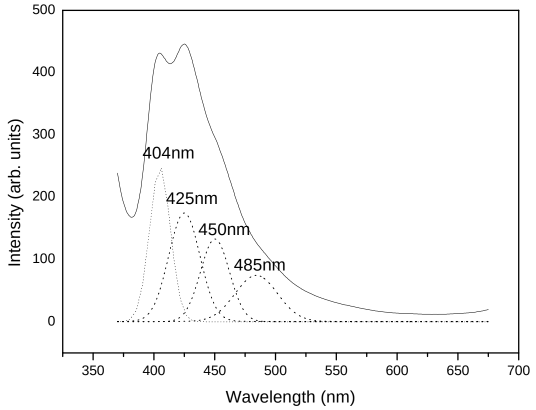

Fig. 4. Room temperature photoluminescence spectra of the Cu doped ZnS nanoparticles. The solid line represents the experimental data whereas the dotted lines are the individual components obtained by Gaussian fitting.

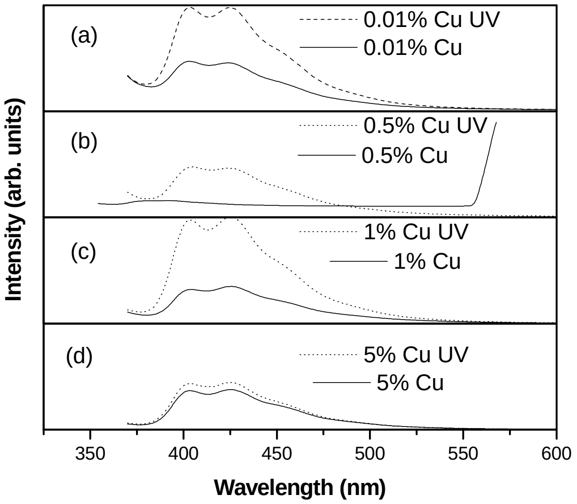

Fig. 5. Room temperature photoluminescence spectra of the ZnS nanoparticles having different Cu^{2+} concentrations (a) 0.01% (b) 0.5 % (c) 1 % (d) 5 %; showing the luminescence enhancement on UV irradiation for each concentration of the dopant.

Remarkable enhancement of the luminescent intensity was observed on irradiating the ZnS:Cu nanoparticles with UV radiation of 255 nm for 24 hours at room temperature. As shown in Fig. 5, there is no shift in the peak position; therefore the increase in luminescent intensity can be attributed to the increase in the radiative transition probabilities [10, 11] of the samples. Possibly on UV irradiation, the photochemical reactions with oxygen might have occurred, leading to the formation of $ZnSO_4$ and/or $Zn(OH)_2$ layer around the ZnS:Cu nanoparticles [3]. This layer could have acted as an inorganic surfactant, leading to the decrease in the number of trap sites available for non-radiative transitions. It has also been observed that the increase in PL intensity is more when the concentration of the dopant Cu^{2+} ions is less as compared to the increased concentration. As shown in Figs. 5 and 6, this enhancement in the PL intensity on UV-irradiation is much more when the dopant concentration is 1% and less; as compared to 3% Cu^{2+} ion concentration. As discussed by W. Q. Peng et. al. [6], the relative intensity of the overall photoluminescence spectra reaches the maximum at the doping concentration of 1%, therefore, the decrease in PL intensity at higher concentrations of the dopant can be attributed to the formation of CuS, though the XRD measurement did not detect its existence. This can also be supported by the change of the color of ZnS:Cu nanoparticles from white to dark green as the concentration of the Cu^{2+} is increased. This CuS formation enhances the non-radiative transitions as well as reduces the number of Cu^{2+} ions, which act as optically active luminescent centers. Now, on UV irradiation, discoloration of the samples has also occurred, which further supports the decrease of non-radiative transitions on account of photo-oxidation reactions and hence the decrease of the non-radiative transition probability.

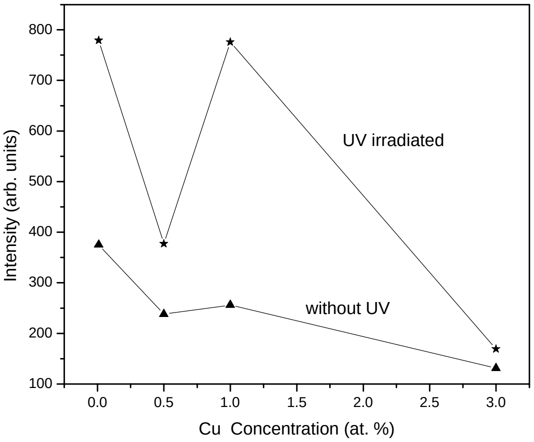

Fig. 6. The plot of PL intensity versus the Cu^{2+} concentration (as added during synthesis) in the ZnS nanoparticles with and without UV irradiation.

5. Conclusion

In short, we have fabricated ZnS:Cu nanoparticles having average diameter ~ 3-5 nm, using chemical precipitation technique. The changes in the optical properties of these nanoparticles with varying concentration of the dopant as well as on UV irradiation have been studied. UV-Visible absorption studies indicate no significant change in the band gap values of the ZnS:Cu nanoparticles on prolonged UV-irradiation. Whereas a slight increase in the band gap values is observed for the nanoparticles (3.78 eV), as compared to the bulk (3.67 eV), on the account of the quantum confinement effect. The PL spectra of the ZnS:Cu samples has been found to be broad and asymmetric and, therefore, it is deconvoluted into three blue luminescence and a blue-green luminescence peak. Remarkable enhancement of the PL intensity has been observed on UV irradiation, which has been attributed to the photochemical reactions, leading to the formation of $ZnSO_4$ and/or $Zn(OH)_2$ layer around the ZnS:Cu nanoparticles. Moreover, as the Cu^{2+} ion concentration is increased (greater than 1%), the decrease in PL intensity is observed and the PL intensity enhancement of UV irradiated samples also decreased. This might be due to the concentration quenching by the formation of CuS compound. The PL intensity as well as the enhancement is maximum in ZnS:Cu (1 %) samples.

These changes can be harnessed to synthesize highly luminescent nanophosphors, which can further be used in fabricating optoelectronic devices.

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