Enhanced photoluminescence properties of ZnS:Cu$^{2+}$ nanoparticles using PMMA and CTAB surfactants

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1. Introduction

Nanotechnology is a broad interdisciplinary area of research, development and industrial activity, which has been growing rapidly world wide for the past decade. Nanoparticles are the end products of a wide variety of physical, chemical and biological processes, some of which are novel and radically different, others are quite common [1,2]. Due to their unique optical properties such as broad excitation band, narrow emission spectrum, size and composition-tunable emission wavelength the nanoparticles were used as an excellent antiphoto bleaching [4,5]. The nanomaterials are known for their unique mechanical, chemical, physical, thermal, electrical, optical, magnetic, biological and also specific surface area properties, which in turn define them as nanostructures, nanoelectronics, nanophotonics, nanobiomaterials, nanobioactivators, nanobiolabels, etc. In the last one decade, a large variety of nanomaterials and devices with new capabilities have been generated by employing nanoparticles based on metals, metal oxides, ceramics (both oxide and non-oxide), silicates, organics, polymers, etc. The considerable progress has been achieved in this field to understand the size related properties in materials. As the size of semiconductor nanoparticles decreases, a threshold value characteristic of each type of semiconductors is reached. At smaller nanoparticle sizes, the energy gap (band gap) increases, and the optical spectrum is shifted toward the short-wavelength region [6].

As a nontoxic II–VI semiconductor material, ZnS is chemically more stable and technologically better than other semiconductor materials (such as ZnSe), it is considered to be a promising host material. Both transition metal ions (e.g. Mn$^{2+}$ [7,8] and Cu$^{2+}$ [9]) have been incorporated into ZnS nanostructures by various physical and chemical methods. These doped ZnS semiconductor materials have a wide range of applications in electroluminescence devices,

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phosphors, light emitting displays, optical sensors, etc. Among these nanostructured materials, zinc sulfide nanoparticles doped with Cu$^{2+}$ ions (ZnS:Cu$^{2+}$) are of special interest due to the highly effective luminescence [10].

Semiconductor nanocrystals capped with organic molecules can have a relatively large number of unpassivated surface sites as it is difficult to passivate both anionic and cationic surface sites simultaneously by these capping groups [11]. These unpassivated surface sites may act as non-radiative recombination centers, which suppress their luminescence. In addition, organically capped nanocrystals have very long emission lifetimes and large Stoke’s shifts [12] whereas inorganically capped nanoparticles exhibit enhanced luminescence efficiencies [13] and shorter life-times [14]. The epitaxial growth of inorganic cap on the nanocrystals can eliminate both the anionic and cationic surface dangling bonds [11]. Inorganic passivation is, therefore, more effective than organic passivation for eliminating surface defect sites. It is reported that fluorescence intensity can be increased by covering the nanoparticle surface with Cd(OH)$_2$ [15]. Zou et al. [12] have studied the effectiveness of various inorganic capping agents having different band gaps on the surface passivation of cadmium sulphide (CdS) nanoparticles.

In this work, PL emission properties of the ZnS samples doped with Cu$^{2+}$ and surfactants capped particles have been presented. The size of the synthesized ZnS:Cu$^{2+}$ samples are in the 3.4–5.2 nm range as has been confirmed from X-ray diffraction (XRD) peak broadening, transmission electron microscope (TEM) micrograph analysis and UV–vis absorption. The optical absorption properties show a blue shift of the absorption edge due to the quantum confinement effect. In the prepared ZnS:Cu$^{2+}$ samples, PL emission takes place covering the whole visible region with the peaks appearing at 472, 484 and 496 nm. The enhancement in the PL emission is observed as compared to that of uncapped ZnS nanoparticles.

2. Experimental

All steps of the synthesis were carried out at room temperature and all chemicals used were AR grade. The water was used as a solvent in the experiments. First, a desired molar proportion of Zn(CH$_3$COO)$_2$·2H$_2$O in 50 ml de-ionized water and Cu II (CH$_3$COO)$_2$·4H$_2$O (wt% in Zn= 0.2%, 0.4%, 0.6% and 0.8%) in 50 ml de-ionized water were dissolved and surfactant was added to control the growth of the nanocrystals during the reaction. Subsequently, the Na$_2$S (50 ml) was added drop wise by an additional funnel to the above mixture. For each experiment, the molar amounts of Zn(CH$_3$COO)$_2$ and Na$_2$S used were equal. Undoped ZnS nanoparticles were synthesized by following the same procedure without doping and capping agents (PMMA and CTAB). For the synthesis of surfactants capped ZnS:Cu$^{2+}$ nanoparticles, the surfactant should be added. During the whole reaction process, the reactants were vigorously stirred under air atmosphere at 80°C. The formed nanocrystals were separated from the solution by centrifuging. After washing repeatedly with deionized water and then drying at 60°C under vacuum, the powder samples of ZnS:Cu$^{2+}$ nanoparticles were obtained.

The X-ray diffraction (XRD) patterns of the powdered samples were recorded using XPERT-PRO diffractometer with a Cu Kα radiation ($\lambda$ = 1.54060 Å) under the same conditions. The crystallite size was estimated using Scherrer’s equation ($0.9\lambda/(\beta \cos \theta)$) at full width at half maximum of the major XRD peak. The size and morphology of the nanoparticles were determined using TEM (PHILIPS-CM200; 20–200 kV). For sample preparation, dilute drops of suspension were allowed to dry slowly on carbon-coated copper grids for TEM measurement. The FT-IR spectra were recorded on an AVATOR 360 spectrometer. The optical transmission/absorption spectra of the same particles in de-ionized water were recorded using UV-1650PC.

Fig. 1. XRD spectra of ZnS, ZnS:Cu$^{2+}$ (0.2–0.8%) and different surfactants capped (PMMA and CTAB) capped ZnS:Cu$^{2+}$ nanoparticles.

SHIMADZU spectrometer. Fluorescence measurements were performed on an RF-5301PC spectrophotometer. Emission (350–650 nm) spectra were recorded under 315, 302 and 294 nm for uncapped, TOPO and SHMP capped ZnS:Cu$^{2+}$ nanoparticles, respectively. The thermal analysis was carried out with SDT Q600 20 thermometer.

3. Results and discussion

3.1. Structure and morphology

Fig. 1 illustrates the XRD patterns of the ZnS, ZnS:Cu$^{2+}$ and surfactants capped ZnS:Cu$^{2+}$ nanoparticles. It shows very broad diffraction peaks, which are the characteristic of nanosized materials. For all the samples three diffraction peak positions correspond to the lattice planes of (1 1 1), (2 2 0) and (3 1 1), which matches very well with the cubic zinc blende structure (JCPDS No. 05-0566). No diffraction peaks from copper impurities were detected. Thus it is observed that the Cu$^{2+}$ ions are dispersed into the ZnS matrix. According to the Debye–Scherrer formula [16], the mean crystalline sizes calculated from the full-width at half-maximum (FWHM) of these lines are about 4.8 and 5.2 nm for uncapped ZnS and ZnS:Cu$^{2+}$ nanoparticles. Further, relatively larger line broadening in surfactant (PMMA and CTAB) capped samples indicates their smaller particle size as compared to uncapped samples. From the XRD line width, the mean crystalline domain sizes have been estimated to be around 3.5 and 4 nm for PMMA and CTAB capped ZnS:Cu$^{2+}$ particles, respectively. This result indicates necessity of the capping agent for the reduction of particles’ size. By comparing the effect of two surfactants, the CTAB is used as an effective surfactant to reduce the particles’ size, which may be due to the presence of the sodium ions in this surfactant.

A typical SEM microphotographs of ZnS and ZnS:Cu$^{2+}$ nanoparticles (Figs. 2 and 3) show that the particles have smooth surface and an
average agglomerate size of around 30 nm. But the actual size of the nanoparticles cannot be determined from the SEM images, as it is limited by the resolution of the used SEM instrument (the actual particle sizes calculated through XRD are diffraction as 4.8 and 5.2 nm). The elemental composition determined through EDX attached with SEM instrument is shown in Figs. 2b and 3b, for ZnS and ZnS:Cu\(^{2+}\) nanoparticles, respectively. This (Fig. 3b) reveals that the Cu\(^{2+}\) ions are incorporated in the Zn\(^{2+}\) lattice sites.

It is necessary to obtain the particle size and information about nanostructures by direct measurement, such as transmission electron microscope (TEM), which can reveal the size and morphology of the particles. Figs. 4 and 5 show TEM images of the PMMA and CTAB capped ZnS:Cu\(^{2+}\) (0.4\%) nanoparticles, respectively. The TEM images indicate, the synthesized particles are spherical in shape and homogeneous distribution. The TEM images of PMMA capped particles reveal the distinct grain boundaries (Fig. 4) with an average crystallite size about 3.5 nm and 4 nm for CTAB capped ZnS:Cu\(^{2+}\) nanoparticles (Fig. 5). This supports, that the size of the synthesized ZnS:Cu\(^{2+}\) nanoparticles are in consistent with XRD result.

Fig. 3. (a) SEM image of ZnS:Cu\(^{2+}\) nanoparticles and (b) corresponding elemental dispersive X-ray spectrum.

Fig. 4. TEM image of PMMA capped ZnS:Cu\(^{2+}\) nanoparticles.

3.2. FT-IR study

Fig. 6 (a–d) shows FT-IR spectra of the ZnS, ZnS:Cu$^{2+}$, PMMA and CTAB capped ZnS:Cu$^{2+}$ nanoparticles. From the FT-IR analysis of uncapped ZnS nanoparticles (Fig. 6 a), the peaks appearing at 1110, 618 and 491 cm$^{-1}$ are due to Zn–S vibrations. The obtained peak values are in good agreement with the reported literatures [16,17]. The peaks at 1133 and 1112 cm$^{-1}$ of Fig. 6 (b) show the presence of the doping ions (Cu$^{2+}$) in ZnS. Moreover, the transmittance peaks of the ZnS:Cu$^{2+}$ are slightly shifted to lower wave number side from the uncapped ZnS, which may be due to the presence of the doping ions. These peaks are slightly shifted to higher wave number side with decrease in intensity when ZnS:Cu$^{2+}$ nanoparticles are capped with surfactants. In the FT-IR spectrum of the composite (Fig. 6c), the absorption bands at 1700–1750 cm$^{-1}$ are the characteristic of C=O stretching vibration of PMMA. In addition, the absorption bands at 1150 cm$^{-1}$, 1191 cm$^{-1}$, 1240 cm$^{-1}$ and 1269 cm$^{-1}$also represent C–O–C stretching vibration of PMMA [18]. The strong peaks observed at 1610 and 1402 cm$^{-1}$ are shifted to long wavenumber side from the uncapped particles (Fig. 6b), which indicates the presence of CTAB on the ZnS:Cu$^{2+}$ surface. The broad absorption peaks for all the samples in the range of 3410–3465 cm$^{-1}$ corresponds to –OH group, which indicate the existence of water absorbed in the surface of nanocrystals. The presence of this band can be clearly attributed to the adsorption of same atmosphere water during FTIR measurements. The bands at 1500–1650 and 2360–2343 cm$^{-1}$ are due to the C=O stretching mode arising from the absorption of atmospheric CO$_2$ on the surface of the nanoparticles [19].

3.3. UV–visible study

The room-temperature UV–visible absorption spectra of freshly-prepared undoped and Cu$^{2+}$ doped ZnS, PMMA and CTAB—capped ZnS: Cu$^{2+}$ nanoparticles (Fig. 7) shows the absorption peak position in the ultraviolet range. The absorption peaks of different concentrations of Cu$^{2+}$ doped ZnS nanoparticles has no change in the peak position (not shown). However, the relative intensity is changed. Among the four different concentrations (0.2–0.8%), the 0.4% of Cu$^{2+}$ doped ZnS gives strong absorption. For this reason, the 0.4% of Cu$^{2+}$ was selected as an optimum concentration for the other study. In addition, the absorption peaks of the surfactant capped particles have no change with respect to the capping concentrations (not shown). But the shifting was observed. As observed in Fig. 7, the samples exhibit the absorption peak at around 310 (4 eV), 315 (3.94 eV), 288 (4.31 eV) and 298 (4.16 eV) nm for ZnS, ZnS:Cu$^{2+}$, PMMA and CTAB capped ZnS:Cu$^{2+}$ nanoparticles, respectively. The absorption peaks of all samples were strong by blue shifted as compared with 345 nm (3.6 eV) of bulk ZnS. This blue shift of the bandgap takes place because of the quantum confinement effect [10]. Comparison of the four absorption values, the PMMA capped ZnS:Cu$^{2+}$ is more blue shifted than the others. It may be due to reduction of the particles’ size. According to Kumbhojkar et al., [20], the properties of nanocrystalline materials show deviation from the corresponding bulk properties when the sizes of the crystallites become comparable to the Bohr excitonic radius. The reported value of Bohr radius of the ZnS is ~2.5 nm [3]. The values of grain size in the nanocrystalline for capped ZnS:Cu$^{2+}$ are almost same as determined

![Fig. 5. TEM image of CTAB capped ZnS:Cu$^{2+}$ nanoparticles.](image1)

![Fig. 6. (a–d) FT-IR spectra of ZnS (a), ZnS:Cu$^{2+}$ (b) and surfactants (PMMA (c) and CTAB (d)) capped ZnS:Cu$^{2+}$ nanoparticles.](image2)

![Fig. 7. UV–vis absorption of ZnS, ZnS:Cu$^{2+}$ (0.4%), and surfactants (PMMA and CTAB) capped ZnS:Cu$^{2+}$ nanoparticles.](image3)
from XRD and TEM studies. It is comparable to excitonic Bohr radius \( a_B \) supporting the quantum–size effect. Further, the grain sizes were calculated using Brus equation. Based on the peak position in the absorption spectrum, the sizes of the nanocrystals have been calculated as 4.9, 5.2, 3.4 and 3.9 nm for ZnS, ZnS:Cu\(^{2+}\), PMMA and CTAB capped ZnS:Cu\(^{2+}\) nanoparticles, respectively. The obtained values are in good agreement with XRD, TEM and also excitonic Bohr radius of bulk ZnS.

3.4. Photoluminescence study

The PL spectra of undoped and various concentrations of Cu\(^{2+}\) doped ZnS nanoparticles recorded at room temperature were shown in Fig. 8a. The excitation of the observed emission peaks under 310 and 315 nm. For the undoped sample (inset in Fig. 8a) a broad emission peak was observed at 445 nm due to donor–acceptor pair [21]. When Cu\(^{2+}\) ions were doped into ZnS nanoparticles, more defect states will be introduced. Therefore, it is reasonable some new peaks had appeared in the longer wavelength side. Comparison of the two spectra, the impurity (Cu\(^{2+}\)) doped ZnS spectra was more red shifted from the undoped ZnS. The spectra show a broad emission spectrum around 400–600 nm. It is in agreement with earlier results in ZnS:Cu\(^{2+}\) nanoparticles [22–25]. Three emission peaks were observed in the blue region, at 472 [26], 484 [27] and 496 nm [22], arises from the recombination between the shallow donor level (sulfur vacancy) and the \( t_2 \) level of Cu\(^{2+}\) [27]. With an increase of the Cu\(^{2+}\) concentration (from 0.4 to 0.6%), the green light position is systematically shifted to longer wavelength (from blue to green (524 nm)) [28]. Moreover, the intensity of the ZnS:Cu\(^{2+}\) emission was decreased by higher concentration of the Cu\(^{2+}\). Fig. 8b shows concentration versus intensity. This illustrates an optimum concentration (0.4%) of doping Cu\(^{2+}\) ions for enhanced PL emission. When Cu\(^{2+}\) ions were incorporated in ZnS host lattice, the luminescence centers of Cu\(^{2+}\) ions are formed. Hence from the PL emission spectra, it can be concluded that the Cu\(^{2+}\) ions are incorporated successfully into the ZnS host lattice.

The enhanced luminescence properties of the capped ZnS:Cu\(^{2+}\) nanoparticles are attributed to the surface passivation of the nanoparticles by PMMA and CTAB capped, which minimize the surface defects and enhance the electron–hole recombination. The emission spectra for both samples appeared in the visible range. Fig. 9a shows a PL spectra of different concentrations of PMMA capped ZnS:Cu\(^{2+}\) nanoparticles. The PL emission contains three peaks at 472, 484 and 496 nm. The peak position has no change with respect to the capping concentrations. However, the relative intensity varies. Moreover, the observed peak position in the PL emission for PMMA capped particles has no change from the uncapped ZnS:Cu\(^{2+}\) (Fig. 8a), but the emission intensity is increased. The PL improvement may be due to the presence of carboxyl group in PMMA. Fig. 9b shows a plot of concentration of PMMA and intensity. As shown in the figure, the emission intensity is increased with respect to concentration of the surfactant (PMMA). It indicates, increase in particles’ growth with respect to the concentration of the PMMA. Fig. 10a shows room temperature photoluminescence of the CTAB capped ZnS:Cu\(^{2+}\) nanoparticles. It is observed that there is no shifting in PL emission with respect to uncapped and PMMA capped ZnS:Cu\(^{2+}\) nanoparticles. However, the PL intensity is enhanced more than two times, this enhancement may be due to the presence the halogen groups (Br) in CTAB. It indicates the improved particles’ growth by adding the CTAB as a surfactant. The PL intensity is increased by increasing the CTAB concentrations (Fig. 10b) up to 1 g after that the intensity is decreased. This decrease may be due to reduction of particles’ growth in colloidal solution. Thus from the overall point of view
the role of the PMMA (\(\sim 3.5 \text{ nm}\)) in this work controls the particles’ size and growth. However, the role of CTAB in controlling the size is seldom than the PMMA, but it excites the particles’ growth, resulting in enhanced PL emission.

3.5. Thermal study

The TG-DTA thermograms were recorded for ZnS:Cu\(^{2+}\) nanoparticles in the temperature range from room temperature (RT) to 1000 °C with an increase by 10 °C/min in air atmosphere. Fig. 11 shows combined plots of TG and DTA. From the TGA data plot, it is noticed that the weight loss of the nanoparticles are found to take place upto 700 °C. For DTA curve, the first endothermic peak was found at 65 °C. This peak is attributed to the evaporation of the water. The endothermic peak around 230 °C probably corresponds to the evaporation of organic and lattice deformation of ZnS:Cu\(^{2+}\). The composition does not vary in the annealing range from 100 °C to 200 °C, whereas, as can be seen, beyond 230 °C, most Cu\(^{2+}\) ions are released from the ZnS matrix. The observed endothermic peak at 330 °C was believed to be the beginning of phase transition. A broad exothermic peak at 400 °C implies the improvement of the crystallinity of the sample. Additionally, above 500 °C, there is a smooth downward trend in DTA curve with significant weight loss. This may be due to release of residual sulfur ions from the sample.

4. Conclusion

The ZnS, ZnS:Cu\(^{2+}\), PMMA and CTAB capped ZnS:Cu\(^{2+}\) nanoparticles were successfully synthesized in aqueous medium at air atmosphere. The particles were stabilized by the steric hindrance to reduce agglomeration. The XRD patterns of the surfactants capped nanoparticles showed the materials were of nanometer size regime with a cubic phase. The particle structure has no change with respect to the concentration of Cu\(^{2+}\) and capping agents. However, size of the particles is changed. The TEM images indicated that the growth particles are spherical in shape and homogeneous dispersion. Prominent IR peaks are identified on ZnS:Cu\(^{2+}\) surface. The particles size was controlled by PMMA and PL intensity was improved by CTAB. The stability of the ZnS:Cu\(^{2+}\) nanoparticles were studied by TG-DTA. The findings demonstrate the
preparation of the monodispersed ZnS:Cu$^{2+}$ nanoparticles, which is a potential application for biological labeling and sensor devices.

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References


