SYNTHESIS, CHARACTERIZATION AND PHOTOCATALYTIC ACTIVITY OF THE SAMARIUM ION DOPED ZnS NANOCLUSTERS

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In the present work, polyvinyl pyrrolidone (PVP) capped Zn\(_{1-x}\)Sm\(_x\)S (0.0001 \(\leq x \leq 0.1\)) nanoclusters were prepared using conventional chemical co-precipitation technique. The synthesized samples were characterized using X-ray powder diffraction (XRD), transmission electron microscope (TEM) and UV-Vis absorption studies. The XRD and TEM studies reveal that the synthesized ZnS nanocrystals have cubic (zinc blende) structure with average crystalline size \(\sim 28\) nm. Photocatalytic activity under ultra violet (UV) light exposure has been studied using methylene blue (MB) dye as test contaminant. A possible mechanism is proposed to explain the charge carrier recombination and interfacial charge transfer processes. It has been found the optimum amount of Sm\(^{3+}\) doping and increased adsorption ability of light due to high separation rate of photoinduced charge carriers, which play an important role in enhancing the overall photocatalytic performance significantly.

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1. Introduction

Synthesis and characterization of wide band gap (~ 3.6 eV) II-VI semiconductor materials have drawn significant attention in the last 10 years. Nanosized semiconductor crystallites exhibit unique chemical, physical and electronic properties, which support their potential applications in opto-electronics, data storage devices, quantum dot lasers, nanosensors, nanophosphors, biological markers and efficient photocatalysts [1-6]. Transition from bulk to nanoparticles lead to the display of quantum mechanical properties and an increased dominance of surface atoms [7-8]. Small sized nanomaterials show large surface area to volume ratio, which leads to high surface reactivity to enhance the chemical reaction dynamics and photon absorption efficiency. In the case of photocatalytic process, the electron-hole pair generated on the surface of semiconductor material by visible or ultraviolet (UV) photon undergoes redox reaction with molecules adsorbed onto the catalyst surface, thereby breaking them into smaller fragments. These processes find their applications for the mineralization of toxic organic compounds, hazardous inorganic constituents and bacteria disinfection. The photocatalytic activity of any semiconductor catalyst strongly depends upon adsorption capacity and the electron-hole pair separation efficiency of the catalyst. The adsorption capacity can be improved by increasing the specific surface area of catalysts. On the other hand, electron–hole separation efficiency could be significantly enhanced by doping the pure catalysts with rare earth and/or transition metals impurities. Doping with rare earth and/or transition metals creates quasi-stable energy states within the band gap and behaves as trap site for electrons and holes. Electron trapping due to higher defect sites leads to increase in the photocatalytic efficiency provided the electron-hole pair recombination rate is lower than the rate of electron transfer to adsorbed molecule.

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During the recent past, various new semiconductor nanomaterials have been synthesized and characterized for their photocatalytic activity. Photocatalytic activity of the anatase form of TiO$_2$ under UV light exposure has been extensively investigated by Li et al. [9]. Choi et al. [10] systematically reported the photoreactivities and transient charge carrier recombination dynamics for TiO$_2$ colloids doped with Fe$^{3+}$, Mo$^{5+}$, Ru$^{3+}$, Os$^{3+}$, Re$^{5+}$, V$^{4+}$ and Rh$^{3+}$ impurities. ZnO has emerged to be an efficient photocatalyst material as compared to other metal oxides [11-14]. Likewise, ZnS [15-16] nanostructures showed unique photocatalytic activity due to rapid generation of electron-hole pairs by photo excitation and the highly negative reduction potentials of excited electrons. Zhao et al. [15] synthesized hierarchical ZnS nanostructures with different sizes and reported that as obtained ZnS structures exhibit potential photocatalytic activity. In the present work, Zn$_{1-x}$Sm$_x$S nanoclusters were successfully prepared by chemical co-precipitation method. Synthesized nanostructures have been characterized using powder XRD, TEM and UV-Vis absorption measurements. A possible mechanism is proposed to explain the charge carrier recombination, charge carrier trapping and interfacial charge transfer processes. Moreover, dependence of photocatalytic activity and luminescence efficiency on the of Sm$^{3+}$ concentration have been described in detail.

2. Experimental procedure

2.1 Synthesis of Sm$^{3+}$ loaded ZnS nanoclusters

Polyvinyl pyrrolidone (PVP) capped Zn$_{1-x}$Sm$_x$S nanoclusters were synthesized using bottom-up wet chemical co-precipitation technique. The aqueous solutions of analytic reagent grade chemicals: zinc acetate (C$_4$H$_6$O$_4$Zn.2H$_2$O), sodium sulphide (Na$_2$S.xH$_2$O), samarium acetate hydrate [(C$_2$H$_3$O$_2$)$_3$Sm.xH$_2$O] and polyvinylpyrrolidone (PVP) [(C$_6$H$_9$NO)$_n$] were used in synthesis without further purification. All chemicals were procured from Sigma-Aldrich, India limited, Mumbai. In a typical synthesis of samarium doped ZnS nanocrystals, 0.5M zinc acetate, 1M samarium acetate, 0.5M sodium sulphide and 2 % PVP were prepared separately in triple distilled water. The zinc and samarium precursor solutions were mixed in the stoichiometric proportion under vigorous stirring. 4 ml of 2% PVP solution was added to total 50 ml volume, before dropwise addition of sulphur precursor. The PVP solution was added to prevent the further growth of nanocrystalline and whole reaction process was carried out at room temperature. Resulting precipitates were centrifuged and dried in vacuum oven for 10-12h continuously. To understand the effect of Sm$^{3+}$ doping, five different samples with different concentration of samarium precursor were prepared.

2.2 Characterization techniques

Crystalline size of the Zn$_{1-x}$Sm$_x$S nanoparticles was determined from XRD spectra recorded using PAN-Analytic X’Pert Pro Powder XRD setup equipped 3050/60 Goniometer and Cu anode X-ray tube. XRD scan for the powder sample was performed in the 20 range 20-80° keeping step size 0.001 for the Cu K X-ray radiation ($\lambda = 1.5418$ Å$^{-1}$) at 40 mA-45 kV generator setting. TEM micrographs were recorded using Hitachi (H-7500) TEM facility available at Panjab University, Chandigarh, India. The optical absorption measurements were carried out using UV-Vis absorption spectrophotometer (Systronic PC based Double Beam Spectrophotometer: 2202).

2.3 Photocatalytic activity measurements

The photocatalytic activity of Zn$_{1-x}$Sm$_x$S nanoclusters was examined by studying the degradation of MB dye (C$_{16}$H$_{18}$ClN$_3$S.2H$_2$O) aqueous solution under laboratory made UV-photoreactor. For a typical photocatalytic experiment, 128 mg of the prepared sample was added to 250 ml of 32 ppm methylene blue aqueous solution. The prepared sample was dispersed under ultrasonic vibration for 10 min. The aqueous suspension was put under constant stirring in dark for 1h, so that the MB dye atoms are adsorbed on the surface of nanocrystals. The stable suspension was then exposed to the UV-radiation with continuous magnetic stirring. About 10 ml
of suspension solution was taken out after every 10 minute of UV light exposure. Each suspension solution was then centrifuged to filter out the nanocrystals. The photo degradation of MB dye mixed with each synthesized samples were examined using UV-Vis absorption peaks.

3. Results and discussions

3.1 Characterization analysis

Fig. 1 shows the XRD pattern of ZnS nanoclusters doped with 10% samarium impurity. The X-ray diffraction peaks at 28.5°, 47.6° and 56.4° correspond to planes <111>, <220> and <311>, respectively. These results clearly confirm the zinc blend crystal structure of the synthesized nanomaterials. Furthermore, the absence of any additional peaks in the XRD pattern indicates that no other impurity phases are observed in the synthesized materials. The crystalline size of the nanostructure was calculated using the Scherrer formula [29],

\[ D = \frac{K \lambda}{\beta \cos \theta} \]  

where \( K \) = constant, \( D \) is the crystalline size, \( \lambda \) is the wavelength of Cu \( K\alpha \) radiation and \( \beta \) is FWHM of the diffraction peak. Using the Scherrer formula for intense peak corresponds to <111> plane, the average crystalline size of the nanomaterial is about ~ 20 nm. The recorded TEM images micrographs [Fig. 2] further confirm the high monodispersion of synthesized nanoparticles with average particle size ~ 28 nm. The average particle size calculated from electron micrographs is in close proximity with average crystalline size measured from XRD patterns.

3.2 Photocatalytic activity

The band gap of the semiconductor becomes larger with decreasing particle size. The levels of the valence band are moderately shifted to lower energies, while those of the conduction band are strongly shifted to higher energies. Thus varying the size of semiconductor particles, it is possible to enhance the redox potential of the valence-band holes and the conduction band electrons. Therefore nanosized semiconductor particles can possess enhanced photoredox chemistry. Depositing or incorporating metal ion dopants into the ZnS particles can influence the performance of these photocatalysts. The doping process also affects the dynamics of electron-hole recombination and interfacial charge transfer. Dopant ions may be adsorbed on the surface; they may be incorporated into the interior of the particles, or may form separate oxide phases. The largest enhancement of activity through doping was found in nanosized particles, in which the dopant ions are located within 1-2 nm of the surface [11].
Present measurements report the photocatalytic activity \( \text{Zn}_{1-x}\text{Sm}_x\text{S} \) nanocrystals by degradation of MB dye under UV light exposure. When a photon of UV light strikes the ZnS cluster surface, an electron (e\(^-\)) from its valence band jumps to the conduction band leaving behind a positively charged hole (h\(^+\)) in valance band. The photocatalytic active centers are formed on the surface of ZnS due to increase negative charge in the conduction band. The valence band hole (h\(^+\)) reacts with the chemisorbed H\(_2\)O molecules to form reactive species such as \( \cdot\text{OH} \) radicals, which subsequently react with dye molecules to cause their complete degradation. In case of \( \text{Zn}_{1-x}\text{Sm}_x\text{S} \) nanocrystals, the Sm\(^{3+}\) ions are absorbed on the surface of ZnS nanoparticles and then combine with the electrons in the conduction band of ZnS nanoparticles to form the corresponding metal. These ions reduce the recombination of h\(^+\) and e\(^-\) and favour the formation of \( \cdot\text{OH} \) radicals. It is proposed that increase in photocatalytic activity with Sm\(^{3+}\) doping can be explained by their ability to trap electrons and generate holes so they act as electron scavengers. The retardation of the electron-hole recombination will increase the photocatalytic efficiency of the ZnS nanocrystals photocatalysts and, consequently, accelerate hydroxyl radical formation which will enhance the rate of MB degradation. Schematic presentation of various above mentioned processes involved in photocatalysis of Sm\(^{3+}\) doped ZnS nanoclusters is shown in Fig. 3.
The UV–vis absorbance spectrum of MB solution shows absorption peaks at 243, 286 and 664 nm. The characteristic absorption peak at 664 nm was used to track the photocatalytic degradation process. Absorption spectra of pure MB dye with and without UV radiation exposure is shown Fig. 4. It can be clearly noticed from the recorded spectra that no significant changes of the concentration of MB after 3 h irradiation (data was not shown), which indicated that pure MB solution cannot be easily degraded by UV light. The absorption spectra of MB dye solution mixed with Zn_{0.99000}Sm_{0.01000}S nanocrystals under different duration of UV-radiation is shown in Fig. 5. It is clear from the Fig. 5 that the absorbance of MB dye decreases by 54% after 80 minute exposure of UV light. The sensitized photodegradation of MB dye in the presence of Zn_{1-x}Sm_xS (0.0001 ≤ x ≤ 0.1) nanocrystals are plotted in Fig. 6. It has been observed that the photocatalytic photodegradation of MB dye

![Absorption spectra of pure MB dye with and without UV radiation.](image1)

![Absorption spectrum of MB dye in presence of Zn_{0.90000}Sm_{0.10000}S nanocrystals under different duration of UV light exposure.](image2)
do not follow any regular trend. However, MB dye is degraded to maximum extent in case of 
Zn$_{0.99000}$Sm$_{0.01000}$S nanocrystals, whereas it is degraded to nearly same minimum extent for Zn$_{1-x}$Sm$_x$S ($x = 0.1$, 0.001 and 0.0001) photocatalyst after 80 min. There could be several reasons for 
the variations in the degradation of MB dye with Sm$^{3+}$ ions concentrations. One reason for 
photocatalytic variation is the location and co-ordination of the dopant ions. The number and the 
lifetime of free carriers (electrons/holes) are particle size- and dopant-dependent. It is clear from 
present measurements, there exist optimal Sm$^{3+}$ concentration (1%) for which photocatalytic 
activity is maximum. The dopant Sm$^{3+}$ impurity serve as shallow trapping sites for the charge 
carriers and increase the photocatalytic efficiency by separating the arrival time of e$^-$ and h$^+$ at the 
surface. If Sm$^{3+}$ can act as a trap for both e$^-$ and h$^+$, at high dopant concentration, the possibility 
of charge trapping is high, and, as such, the charge carriers may recombine through quantum 
tunnelling. Therefore the competition between the charge carrier recombination and charge carrier 
trapping followed by the competition between recombination of trapped carriers and interfacial 
charge transfer determine the overall quantum efficiency for interfacial charge transfer.

4. Conclusions

In the present measurements the photocatalytic and optical properties of ZnS nanoclusters 
doped with Sm$^{3+}$ are reported first time. The preliminary results suggested that ZnS:Sm 
nanoclusters exhibit enhanced photocatalytic activity and can be efficiently used for environmental 
cleaning, water purification and H$_2$ production.

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References