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Green synthesis of pure and doped semiconductor nanoparticles of ZnS and CdS

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Abstract: Nanoparticles of pure and Cu/Ag-doped CdS and ZnS have been synthesized via chemical bath deposition without using any capping or toxic reagents. The synthesis was carried out through a simple and less expensive green method. The XRD result shows that both pure CdS and ZnS and their doped derivatives are of high crystalline with hexagonal packing structure. The average crystalline size of all nanoparticles was calculated using Debye−Scherrer formula. The crystalline size of nanoparticles of pure samples varied with that of the doped sample. The average crystalline sizes of all nanoparticles are found to be in the range of 5.5−2.2 nm for CdS (from pure to doped) and 4.3−3.4 nm for ZnS, respectively. The band gap values obtained from UV-visible spectra are in the range of 3.5−2.1 eV for CdS and 3.3−2.7 eV for ZnS derivatives, respectively. The FTIR spectral data give characteristic peaks for Cd—S, Cu—S, Ag—S and Zn—S bonds and confirm the formation of respective nanoparticles. The peaks corresponding to the microstructural formation are also observed. The FE-SEM images show the granular morphological structure for all the samples. The agglomeration size of the samples in the range of 10−50 nm for CdS:Cu and 50−100 nm for ZnS:Cu is observed.

Key words: chalcogenide; ZnS; CdS; nanostructure; semiconductor; green synthesis; catalytic properties

1 Introduction

ZnS and CdS nanoparticles which belong to II−VI group semiconductor compounds are materials having various applications [1−3]. The increased presence of nanomaterials in commercial products such as cosmetics and sunscreens, dental fillings, photovoltaic cells and water filtration and catalytic systems has resulted in a growing public debate on the toxicological and environmental effects of direct and indirect exposure to these materials. Semiconductor quantum dots, also referred to as semiconductor nanocrystals, are a significant class of materials in which quantum confinement effects are investigated in greater detail [4].

Cadmium sulphide is a II−VI group semiconductor compound with direct band gap of 2.42 eV and has interesting optical and electrical properties [5]. It is n-type in nature. Electron-hole pairs generated in CdS are well separated with electrons being highly localized. Cadmium sulphide is the most studied nanocrystalline semiconductor as a photo-anode in photoelectrochemical (PEC) solar cells because of its suitable band gap [6]. CdS shows antibacterial activity [7] and has many applications in photovoltaics [8]. The characteristics of CdS nano particles can be modified to some useful extent by doping with Cu and Ag. Copper impurities behave as acceptor in CdS, change the resistivity, band gap energy, photoelectrical properties and the type of semi-conductivity (from n-type to p-type) [9]. Doping with Ag can provide a convenient way to tailor the physical properties of the intrinsic semiconductor such as photocatalysis [10].

ZnS belongs to II−IV group material with large direct band gap, from 3.4 to 3.70 eV, depending upon composition [11]. It is a potentially important material to be used as an antireflection coating for hetero-junction solar cells [12], for light emitting diode and optoelectronic devices such as blue light emitting diodes, electro luminescence devices [13] and photovoltaic cells which enable wide applications in the field of displays, sensors and lasers. Therefore, much effort has been made to control the size, crystallinity and morphology of ZnS nanoparticles. The Cu-doped ZnS has good luminescent properties [14] and the Ag-doped ZnS has large applications in nano-scale optics [15].

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Many methods such as pulsed laser deposition, sputtering, molecular beam epitaxy, spin coating, spray pyrolysis, chemical bath deposition, are used for the synthesis of semiconductor nanoparticles. In the present study, pure and Cu and Ag incorporated CdS and ZnS nanoparticle have been synthesized by chemical bath deposition (CBD) technique.

2 Experimental

2.1 Materials

The chemicals used in the present study, cadmium chloride ($CdCl_2$), sodium sulphide (Na_2S), copper sulphate ($CuSO_4$), silver nitrate ($AgNO_3$), zinc sulphate ($ZnSO_4$) and thiourea [$CS(NH_2)_2$], were analytical grade reagents of Merck (India) with purity >99.99%.

2.2 Synthesis of nanoparticles

CdS nanoparticles were synthesized by mixing 20 mL solutions each of cadmium chloride and sodium sulphide. The pH of the solution was maintained at 4 by adding HCl and stirred well for 1 h. The precipitated yellow-orange CdS nano-particles were filtered off, washed with distilled water and dried at room temperature. The bath solution used for the deposition of copper incorporated CdS nanoparticles was a mixture of 20 mL of cadmium chloride, 10 mL of copper sulphate and 20 mL of sodium sulphide. All other parameters such as deposition time and pulse rate were kept the same as used for deposition of CdS nanoparticles. The bath solution used for the deposition of silver incorporated CdS nanoparticles was the same as described above except that silver nitrate was used instead of copper sulphate. ZnS and Cu and Ag incorporated ZnS nanoparticles were prepared in the same way except that the cadmium chloride and sodium sulphide were replaced by zinc sulphate and thiourea, respectively. However, in this case, the pH of the solution was maintained at 10 by adding NaOH.

2.3 Structural characterization

The nanoparticles were firstly characterized using XRD for phase analysis. The X-ray analysis was done using a X-ray powder diffractometer with Cu K_α radiation (λ=1.5418 Å) over a range of 20°<2θ<80°. The operational voltage and current were kept at 40 kV and 40 mA, respectively. The optical studies of pure and Cu/Ag-doped CdS, ZnS nanoparticles were carried out using a UV-visible spectrophotometer (model: JASCO V−570) in the wavelength range of 300−800 nm. The morphology of the samples were observed in a Hitachi S−4800 field scanning electron microscope (FE-SEM). All the samples were dispersed in acetone and the diluted samples were drop cast on the two way sticking carbon tape. The metal− sulphide bonds were characterized using IR spectroscopy.

3 Results and discussion

3.1 XRD analysis

The XRD patterns of CdS and Cu and Ag incorporated CdS nanoparticles prepared by chemical bath deposition are presented in Fig. 1. It is observed that the XRD patterns of all samples studied were of similar nature. The peak intensities closely matched with the CdS hexagonal (002) crystalline phase. These results are in agreement with the standard XRD results for these types of nanoparticles.

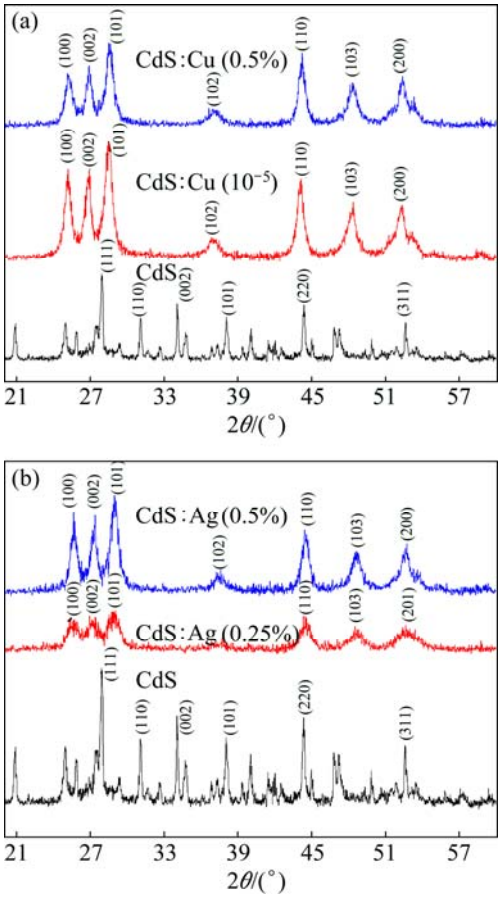

Fig. 1 XRD patterns of CdS and Cu and Ag incorporated CdS nanoparticles

The nanoparticles exhibit that the Miller indices match well with JSPDS card No.06—0314 for cadmium sulphide and the peaks are broadened with the increase in the content of incorporation of Cu and Ag. No characteristic peak was observed for the incorporation of copper. The average crystalline size of all nanoparticles has been calculated using the Debye−Scherer formula:

$D_v=K\lambda/(\beta\cos\theta)$

where D_v is the volume of weighted crystallite size, K is the Scherrer constant (somewhat arbitrary value that falls in the range of 0.87−1), λ is the wavelength of X-ray radiation, β is the integral breadth of a reflection located at 2θ (in radians). The crystalline sizes of CdS and Cu and Ag incorporated CdS nanoparticles obtained from XRD analysis are given in Table 1. It is interesting to observe that the crystalline size of CdS nanoparticles is decreased with the incorporation of Cu [9], but the size is increased with the increase in the concentration of Cu. Similar results were reported for Ag-doped CdS nanoparticles [10].

Table 1 Crystal structure and crystalline size of CdS and Cu and Ag incorporated CdS nanoparticles

Sample	Crystal structure	Crystalline size/nm
CdS	Hexagonal	5.5
10×10^{-6} Cu incorporated CdS	Hexagonal	3.67
0.5% Cu incorporated CdS	Hexagonal	3.95
0.25% Ag incorporated CdS	Hexagonal	2.22
0.5% Ag incorporated CdS	Hexagonal	3.77

The XRD patterns of ZnS [12] and Cu and Ag incorporated ZnS thin films are shown in Fig. 2. A comparison between experimental data with those of standard JCPDS (No. 39—1363) clearly shows that both ZnS and ZnS:Cu nano-crystals obtained in this work have hexagonal structure [14]. The broadening of the peaks can be attributed to the nano sized nature of the sample (Table 2). It should be noted that, the pure ZnS nanoparticles exhibit higher diffraction intensity compared with the Cu/Ag-doped ZnS nanoparticles with well developed different peaks, indicating improved crystallinity [15].

The structure of ZnS nanoparticles remains virtually unchanged by the incorporation of the dopants. In all patterns, no peaks were detected corresponding to impurities. The structural characterizations of the nanoparticles through XRD reveal that the prepared samples are nano-crystalline in nature and their particle size decreases while doping. However, it is found that an increase in the concentration of Cu/Ag decreases the size of nanoparticles.

3.2 UV-visible spectroscopy

The UV-visible spectra of pure CdS [16] and Cu/Ag-doped CdS nanoparticles are shown in Fig. 3. The doping Cu was found to act as a donor [9]. Consequently, the band gap decreases on doping and it results in the increased conductivity of the semiconductor. The doping Ag will act as an acceptor [10] and the conductivity was found to be increased (Table 3).

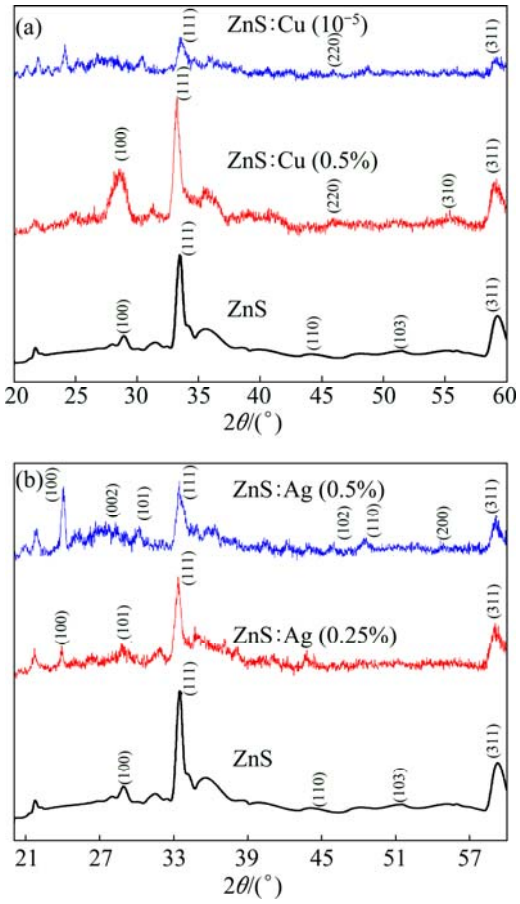

Fig. 2 XRD patterns of ZnS and Cu and Ag incorporated ZnS nanoparticles

Table 2 Crystal structure and crystalline size of ZnS and Cu and Ag incorporated ZnS nanoparticles

Sample	Crystal structure	Crystalline size/nm
ZnS	Hexagonal	4.26
10×10^{-6} Cu incorporated ZnS	Hexagonal	3.45
0.5% Cu incorporated ZnS	Hexagonal	4.06
0.25% Ag incorporated ZnS	Hexagonal	3.45
0.5% Ag incorporated ZnS	Hexagonal	3.61

The spectra of pure ZnS and Cu/Ag-doped ZnS nanoparticles are shown in Fig. 4. ZnS nanoparticles can be considered as a p-type semiconductor when doped with metals [17]. The doping Cu [14] or Ag [15] will act as a donor. The band gap decreases on doping which results an increase in conductivity of the semiconductor (Table 4).

According to quantum size effect, the size of nanoparticle is inversely proportional to the band gap. But here we could not observe such a correlation, which may be due to the fact that both the parent and doping material have absorbance in the UV-visible region and the material is a semiconductor. In addition to the

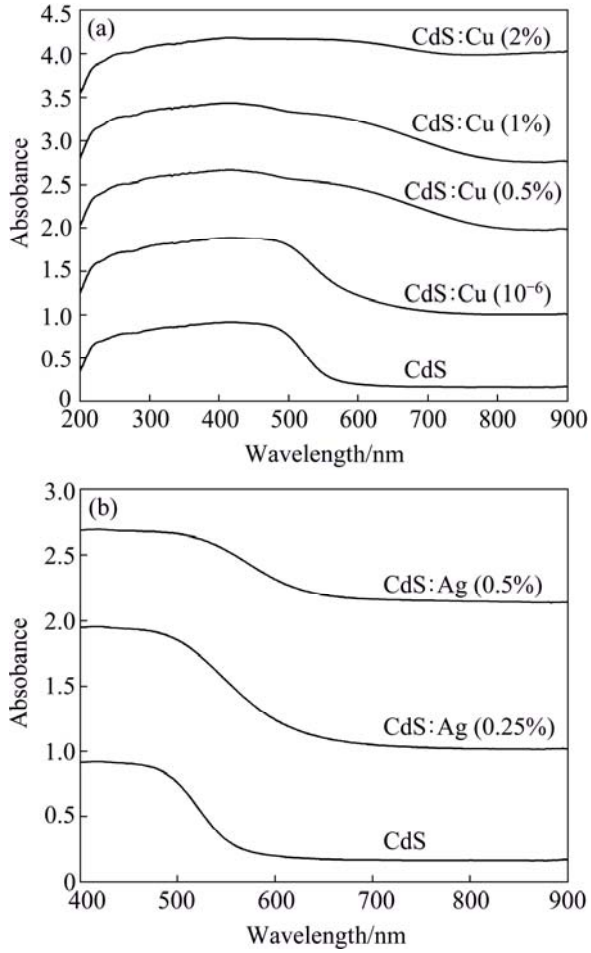

Fig. 3 UV-visible spectra of pure and Cu/Ag-doped CdS nanoparticles

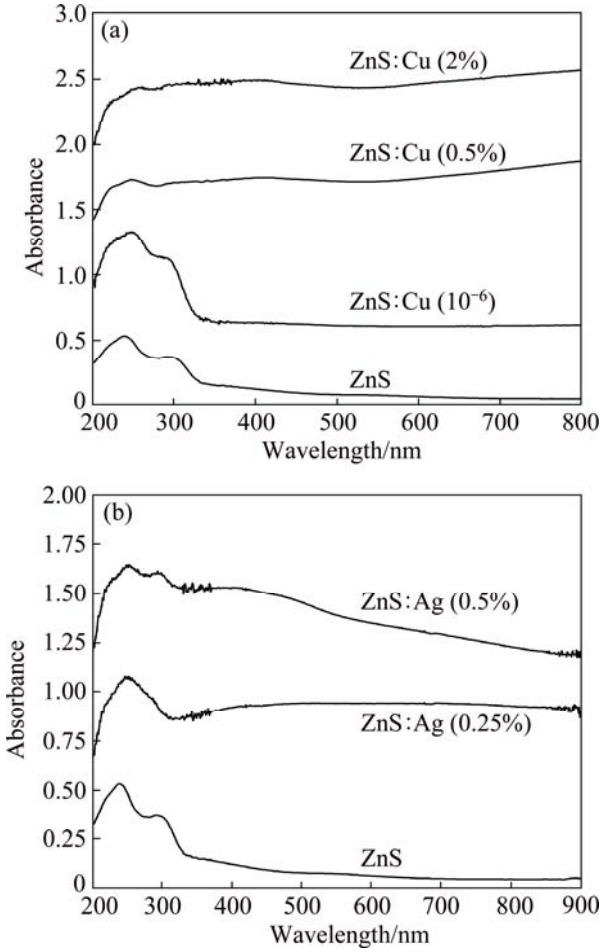

Fig. 4 UV-visible spectra of pure and Cu/Ag-doped ZnS nanoparticles

Table 3 Data obtained from UV-visible spectral analysis of CdS and Cu and Ag incorporated CdS nanoparticles

Sample	Band gap/eV	Crystalline size/nm
CdS	2.56	5.5
10×10^{-6} Cu incorporated CdS	2.52	3.67
0.5% Cu incorporated CdS	2.27	3.95
1% Cu incorporated CdS	2.19	
2% Cu incorporated CdS	2.06	
0.25% Ag incorporated CdS	2.46	2.217
0.5% Ag incorporated CdS	2.37	3.77

Table 4 Data obtained from UV-visible spectral analysis of ZnS and Cu and Ag incorporated ZnS nanoparticles

Sample	Band gap/eV	Crystalline size/nm
ZnS	3.37	4.26
10×10^{-6} Cu incorporated ZnS	3.11	3.45
0.5% Cu incorporated ZnS	3.02	4.06
1% Cu incorporated ZnS	2.94	
2% Cu incorporated ZnS	2.85	
0.25% Ag incorporated ZnS	2.99	3.45
0.5% Ag incorporated ZnS	2.79	3.61

particle size, the concentration of electro-hole pair also affects the band gap. This is the reason for the decrease of band gap on doping. But with the increase of the concentration of dopant, the particle size decreases and thus band gap increases.

3.3 IR spectroscopy

The presence of metal−sulphur bonds in the nanoparticles was identified with the help of IR spectral data. The experimental data were in good agreement with theoretical values. In CdS nanoparticles, the Cd—S vibrations were observed in the range of 400−650 cm^{-1} [5]. In the IR spectra of ZnS nano-particles, we observed peaks at 1120, 617 and 464 cm^{-1} due to Zn—S vibrations [18] and at 2924, 2850, 2364 and 1624 cm^{-1} due to microstructural formations [19]. Peaks observed at 1120 and 1110 cm^{-1} were due to the presence of Cu and the Ag—S vibrations are at 400−550 cm^{-1}.

3.4 Scanning electron microscopy

FE-SEM analysis is a high magnification imaging process mainly used to study the surface morphology of materials. The FE-SEM image imparts information pertaining to the morphology via grain size, shapes, grain boundary and their uniformity. The FE-SEM image for CdS powder with 0.5% Cu is shown in Fig. 5. It shows irregular shapes of particles, made by the aggregation of small particles. The agglomerates show the dimensions in the range of 10−50 nm.

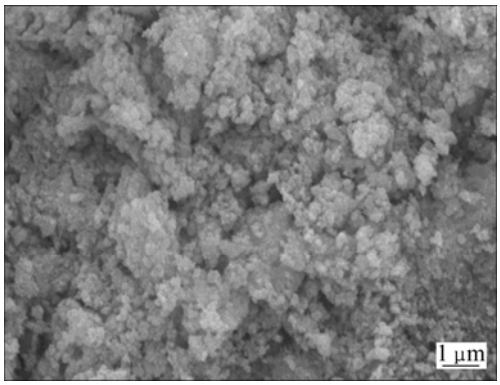

Fig. 5 SEM image of Cu-doped CdS nanoparticles

The FE-SEM images for ZnS powder with 0.5% Cu (Fig. 6) show irregular shaped particles, made by the aggregation of small particles. The agglomerates show the dimensions in the range of 50−100 nm.

4 Conclusions

Pure CdS and ZnS and Cu and Ag incorporated CdS and ZnS have been successfully synthesized via chemical bath deposition technique. As the technique used for the synthesis is low cost and less time consuming and does not produce any harmful pollutants, this method can be attributed as green. The XRD result shows that the powders were of high crystalline in nature. The peaks are found to be broadened with the increase in the concentration of Cu/Ag; however, no characteristic peak was observed due to the incorporation of copper/silver. The average crystalline sizes of all nanoparticles are found to be in the range 5.5−2.2 nm (from pure to doped) and 4.3−3.4 nm for ZnS. The UV-visible spectra give the information about optical properties of nanoparticles. On doping, the band gap decreases and it results in the increased conductivity of the semiconductor. The characteristic peaks observed for Cd—S, Cu—S, Ag—S and Zn—S in the FTIR spectra confirm the formation of respective nanoparticles. The peaks corresponding to the micro structural formation are also observed. The FE-SEM image of CdS:Cu shows same granular morphological structure for all the samples and ZnS:Cu shows an irregularly shaped particles, which may be due to the aggregation of small particles. The agglomerates show the dimensions in the range 10−50 nm for CdS:Cu and 50−100 nm for ZnS:Cu.

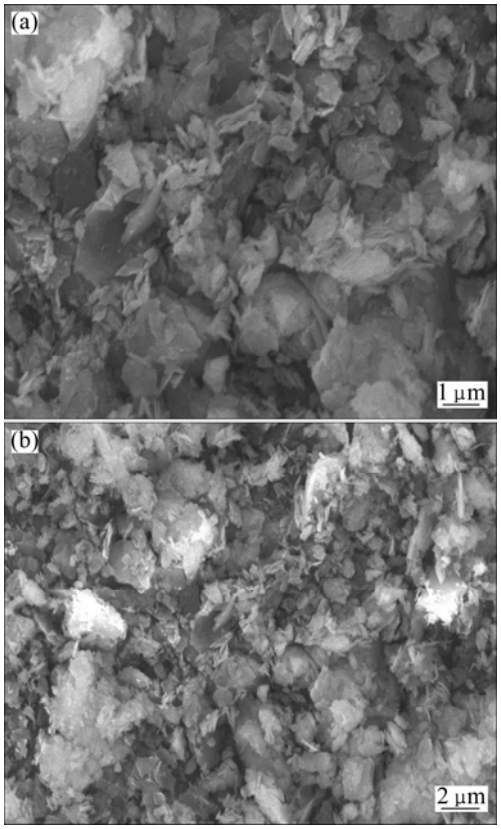

Fig. 6 SEM images of Cu-doped ZnS nanoparticles

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纯 ZnS、CdS 及其掺杂半导体纳米颗粒的绿色合成

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摘　要：采用化学水浴沉积方法制备纯 ZnS、CdS 及 Cu 或 Ag 掺杂 ZnS、CdS 纳米颗粒，整个过程没有使用任何覆盖剂和有毒化学试剂。该制备方法是一种简单的低成本绿色合成方法。XRD 结果表明，所得纯 ZnS、CdS 及其掺杂体结晶良好，具有密排六方结构。采用 Debye−Scherrer 公式计算所有纳米颗粒的平均晶粒尺寸，发现未掺杂纳米颗粒的晶粒尺寸与掺杂样品的晶粒尺寸存在差别。CdS 纳米颗粒的晶粒尺寸为 5.5~2.2 nm，而 ZnS 纳米颗粒的晶粒尺寸为 4.3~3.4 nm。紫外−可见光谱分析表明，CdS 的能带宽为 3.5~2.1 eV，ZnS 的能带宽为 3.3~2.7 eV。FTIR 光谱中存在 Cd—S、Cu—S、Ag—S 和 Zn—S 的特征峰，表明样品中存在这些纳米颗粒。同时还观察到了与显微组织相应的峰。FE-SEM 结果表明，所有样品都具有球状形貌。CdS:Cu 和 ZnS:Cu 纳米粒子发生团聚，其尺寸分别为 10~50 nm 和 50~100 nm。

关键词：硫化物；ZnS；CdS；纳米结构；半导体；绿色合成；催化性能

(Edited by Yun-bin HE)