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Investigation of New Optical Properties of Cd and Co-doped Ag_2S Colloidal Solution

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Abstract

In this work we report new optical properties of the Cd and Co-doped Ag_2S colloidal solution. Cd and Co-doped Ag_2S nanoparticles were prepared using a wet chemical method. The influence of doping on the optical properties of Cd and Co-doped nanoparticles was investigated. The TEM images showed the shape of samples is spherical of average particle size of about 6-18 nm for all pure and doped Ag_2S nanoparticles. The absorption spectra of the doped samples are red shifted as compared with of the pure Ag_2S samples. The Pl intensity of the Cd-doped Ag_2S nanoparticles decreased as Cd concentration was increased. However, the Pl intensity of the Co-doped Ag_2S reduced as the concentration of Co is enhanced. The particle sizes as calculated from the absorption spectra were in agreement with the results obtained from TEM.

Keywords: Metal (Cd,Co); Doped-Ag_2S; Optica; Photoluminescence

Introduction

It is well known that the chemical composition, shape and size-controlled the properties of semiconductor nanostructured materials [1-6]. Semiconductor nanostructured revealed a good electric, magneto-optical and photochemical properties and greatly differing from those observed in the exact bulk materials due to quantum size effects, resulting from a predominant number of surface atoms in Nano size materials [7,8]. Transition metal chalcogenides are very important semiconductor materials, especially in Nano size because of their excellent photoelectron transformation properties and potential application in physics, chemistry, biology, medicine and materials science and their different interdisciplinary fields, for instances solar cells, sensitive sensor, photon computer, and slow release medicament [9]. The Ag_2S is found to be amongst the most important chalcogenides and because of its good optoelectronic properties. Ag_2S nanoparticles have been widely investigated due to its many valuable applications in optical and electronic devices [10-14]. Ag_2S has a direct band gap (0.9-1.05 eV),

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mutually large absorption, useful optical limiting, and considerable chemical stability properties [15,16]. Different synthetic methods have been explored to prepare Ag_2S nanoparticles, such microemulsions [17], sol-gel, ion implantation techniques [18], template [19], the sonochemical way [20], gamma-irradiation [21] and organic-metallic precursor [22]. Semiconductor Nanocrystals doped with metals turn out new opportunities for luminescent [23] because of the formation of the additional electronic levels among the band gaps and also the modification of the band structure. There are few reports on the investigation of the optical properties of Cd and Co-doped Ag_2S nanoparticles in the literature; Ali Fakhri et al., [24] synthesized the Cu doped Ag_2S nanoparticles by the aids of simple chemical co-precipitation method. The TEM images showed the products are a spherical shape in with diameter size of 30 nm and the Pl consequence confirmed that the change of emission wavelength is almost between 456 nm and 477 nm. E.S. Aazam prepared Ni-doped Ag_2S by using a hydrothermal method and he studied the impact of Ni dopant material on the photocatalytic pastime of Ag_2S [25].

The present work focuses on synthesizing the Ag_2S nanoparticles doped with Cd and Co by a wet chemical method and their optical properties were presented for the first time in this study.

Experiential Part

Synthesis

Silver sulfate (Ag_2S), cadmium sulfate ($CdSO_4.8H_2O$), cobalt sulfate ($CoSO_4.7H_2O$) and sodium sulfide ($Na_2S.\ xH_2O$) were obtained from Merck and used as precursors. The chemical reagents were of analytical reagent grade and used without further purification. All the glass wares used in this experimental work were acid washed. Distilled water was used for all dilutions and sample preparations. A pure colloidal solution of Ag_2S nanoparticle was prepared by a wet chemical method. Initially, 0.1 mmol of $AgNO_3$ was dissolved in 50 ml of distilled water. The obtained solution was added dropwise into 50 mL of 0.1 M Na_2S solution with stirring until a transparent pale yellow color solution is obtained. The Cd and Co-doped Ag_2S colloidal solution were prepared by adding 25 ml aqueous solution of 0.001M Na_2S dropwise to a mixture solution of 25 ml of 0.001M solution of Ag_2SO_4 and 25 ml of 0.001M solution of $CdSO_4.8H_2O$ or $CoSO_4.7H_2O$ with stirring until transparent clear solution is obtained. The colors of solutions depend on the amount and type of dopant. Finally, the prepared colloidal solutions of Ag_2S nanoparticles were used for all measurements.

Instrumentation

UV-vis absorption spectra were collected using a UV-vis spectrophotometer (Shimadzu, UV-2400) in the wavelength range from 200 nm to 700 nm. PL spectra were recorded with a spectrofluorometer(JASCO, FP-6500); the extinction wavelength was selected to be 350 nm for Cd-doped Ag_2S and 250 nm for Co-doped Ag_2S nanoparticles. The Transmission Electron Microscopy (TEM) analysis was done with JEM 2010 (JEOL) transmission electron microscope.

Results and Discussion

FIG. 1 (a-c) indicates the morphology and histograms of un-doped, 6% Cd and 6% Co-doped Ag_2S nanoparticles. Spherical to ellipsoid-shaped particles were formed. **FIG. 1 (a-c)** shows the histograms of pure, Cd-doped Ag_2S and Co-doped Ag_2S nanoparticles with the average size of the individual particle in different dopants is in 6-18 nm.

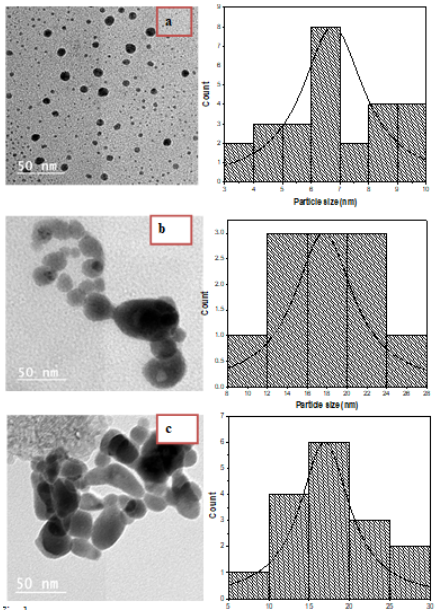

FIG. 1. **TEM images and histograms, a:Undoped Ag_2S, b:6% Cd-doped Ag_2S and c:6% Co-doped Ag_2S.**

A UV-vis spectrum analysis study is a powerful technique for studying the influence of doping on the optical properties of Ag_2S nanoparticles [26,27]. The absorption spectra of corresponding pure and Cd-doped in Ag_2S nanoparticles is illustrated in **FIG. 2.** The UV-vis spectra displayed continuous absorbance increasing from 230 nm to 800 nm. The optical absorption edge of Ag_2S nanoparticles is shifted towards the longer wavelength region with increase the Cd concentration as shown in **FIG. 2**.

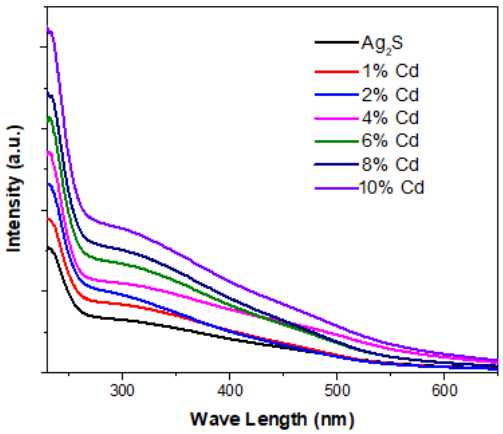

FIG. 2. **UV-vis spectra of Cd-doped Ag_2S nanoparticles.**

The optical band gap energies of different dopants are estimated by Tauc's relation given as below [28]:

$$(\alpha h\nu)^{\frac{1}{n}} = A(h\nu - E_g) \qquad (2.3)$$

Where A is the constant and E_g is the band gap energy of the material. The direct band gap of the samples are calculated by plotting $(\alpha h\nu)^2$ versus $h\nu$ and then extrapolating the straight portion of the curve on the $h\nu$ axis at $\alpha=0$. The straight lines plots shown in **FIG. 3** imply that the Cd-doped Ag_2S samples have direct energy band gap and the band gap was present between 2.62 to 2.27 eV.

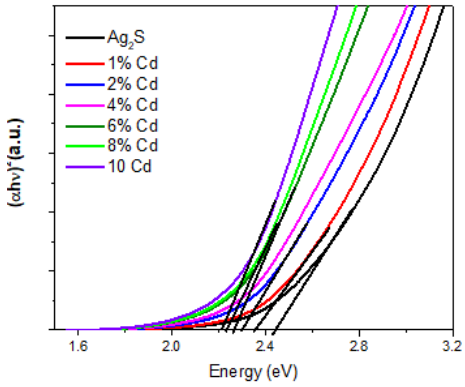

FIG. 3. **Optical band gap spectra of Cd-doped Ag_2S nanoparticles.**

It is clear that the energy gap decreased with the increase in the Cd ions (**FIG. 3**). This red shift is attributed to increase in the particle size which causes to change in particle energy levels and finally decrease the band gap and redshift occurrence. A similar type of decrease was reported on Cd-doped CdS [29]. The size-dependent of band gap energy of Cd-doped in Ag_2S may be obtained using an effective mass approximation as the following equation.

$$E_g \cong E_g^{bulk} + \frac{\hbar^2\pi^2}{2er^2}\left(\frac{1}{m_e m_0} + \frac{1}{m_h m_0}\right) - \frac{1.8e}{4\pi\varepsilon\varepsilon_0 r} \qquad (2)$$

Where E_g^{bulk} is the bulk band gap (eV), ħ is Planck's constant, r is the particle radius, me is the electron effective mass, mh is the hole effective mass, mo is the free electron mass, e is the charge on the electron, ε is the relative permittivity, and εo is the permittivity of free space. Generally, it is accepted that in Ag_2S E_g^{bulk} =1.0 eV, m_e=0.22 m_0 and m_h=1.096 m_0 are, correspondingly, the electron and hole effective masses [30], ε=5.95 is the permittivity [31]. The band gap values of the particles formed with various concentration of the cadmium and the particle sizes calculated using the eq (2) are given in **TABLE 1.**

TABLE 1. **Band gap values of the particles formed with various concentration of the cadmium and the particle sizes.**

Concentration	Energy gab (ev)	Particle size (nm)
0.00	2.6	5.81
0.01	2.54	7.08
0.02	2.45	9.46

0.04	2.36	11.22
0.06	2.31	13.16
0.08	2.29	14.26
0.10	2.27	15.8

It is clearly seen that the band gap energy decreased with increasing the particle size due to the quantum size confinement (**FIG. 4**). These are in good agreement with the values from TEM. The above results indicate that the dimension of the produced Cd-doped Ag_2S nanoparticles and their corresponding optical properties could be controlled by the synthesis method.

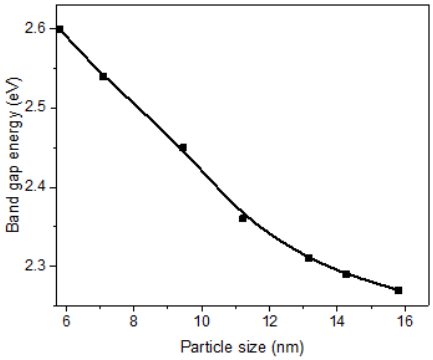

FIG. 4. **Variations of band gap energy with a particle size of Cd-doped Ag_2S nanoparticles.**

FIG. 5 displays the room temperature optical absorption spectra of the pure Ag_2S and Co-doped Ag_2S nanoparticles. On substitution Co to Ag_2S, the absorption band shifts to red, indicating a decrease in the band gap energy from 2.42 to 2.16 eV (see **FIG. 6**). The decrease in the band edge is a clear indication for the incorporation of Co inside the Ag_2S lattice [27,29]. The redshift of band edge for the cobalt doped samples clearly indicates that Co ions are incorporated into the Ag_2S lattice [27]. The band gap values of the Co-doped Ag_2S nanoparticles formed with various concentration of the cobalt and the particle sizes estimated using the eq (2) are given in **TABLE 2**.

TABLE 2. **The band gap values of the Co-doped Ag_2S nanoparticles formed with various concentration of the cobalt and the particle sizes.**

Concentration	**Energy gab (ev)**	**Particle size (nm)**
0.00	2.6	5.81
0.01	2.54	7.08
0.02	2.45	9.46
0.04	2.36	11.22
0.06	2.31	13.16
0.08	2.29	14.26
0.10	2.27	15.8

The variation of band gap energy with the particle size is shown in **FIG. 7**. It is clearly seen that the band gap energy decreased with increasing the particle size as a result of the quantum size confinement. The particle size of Co-doped Ag_2S was estimated from Brus equation, which matches TEM result.

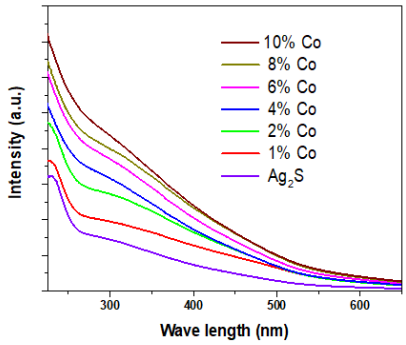

FIG. 5. **UV-vis spectra of Co-doped Ag_2S nanoparticles.**

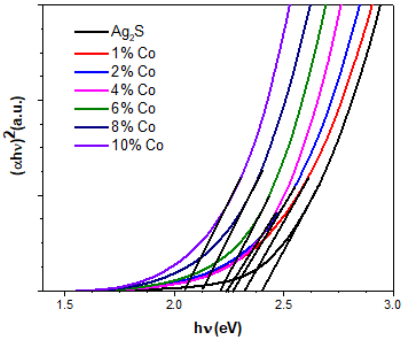

FIG. 6. **Optical band gap spectra of Co-doped Ag_2S nanoparticles.**

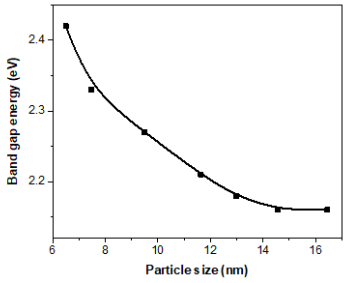

FIG. 7. **Variations of band gap energy with a particle size of Co-doped Ag_2S nanoparticles.**

The PL of the pure Ag_2S and Cd-doped Ag_2S nanoparticles is studied at room temperature to further investigate the optical properties. **FIG. 8** shows the emission spectra of pure and Cd-doped samples (excitation at 350 nm). The spectrum exhibits a broad emission peaks at about 708 for undoped Ag_2S, 710 for 1% Cd-doped Ag_2S, 711 nm for 2% Cd-doped Ag_2S, 713 nm for 4% Cd-doped Ag_2S, 715 nm for 6% Cd-doped Ag_2S, 716 nm for 8% Cd-doped Ag_2S and 718 nm for 10% Cd-doped

Ag_2S. The strong PL peaks may correspond to crystalline defects induced during the growth. Visible emissions are referred to as deep-level emission and are due to the recombination of electrons deeply trapped in silver interstitials and oxygen vacancies, with photo-generated holes [32]. It is clear that the Pl intensity decreased when the dopants of Cd increased. Cd acts as a trapping site, which captures photogenerated electrons from the conduction band, thus separating the photogenerated electron-hole pairs. It is generally accepted that the incorporation of noble metal nanoparticles into Ag_2S [33] enhances the light absorption of the Ag_2S nanoparticles in the visible-light region. This effect leads to a shift in the absorption edge toward longer wavelengths, which indicates a decrease in the band gap energy. This effect leads to a shift in the absorption edge toward longer wavelengths, which indicates a decrease in the band gap energy, which is confirmed by UV-vis spectra measurements.

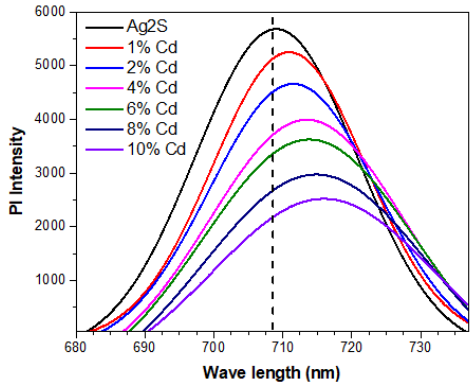

FIG. 8. **PL spectra of Cd-doped Ag_2S nanoparticles.**

A similar photoluminescence spectrum was observed for the Co-doped Ag_2S nanoparticles as (excitation at 250 nm) seen in **FIG. 9**. The emission peak in the visible region at 513 nm, 515 nm, 516 nm, 517 nm, 518 nm, 519 nm, and 520 nm are observed for pure and 1%, 2%, 4%, 6%, 8%, 10% Co-doped Ag_2S. **FIG. 7** also shows that the intensity of these peaks also increases with the doping of Co into Ag_2S nanoparticles. A redshift is seen in PL spectra towards higher wavelength after doping Co into Ag_2S lattice. An increase within the intensity of the deep trap emission of Co-doped Ag_2S is noticed with increasing the concentration of Co. The presence of Co has been reported to enhance the intensity of deep trap emission of bulk Ag_2S [34].

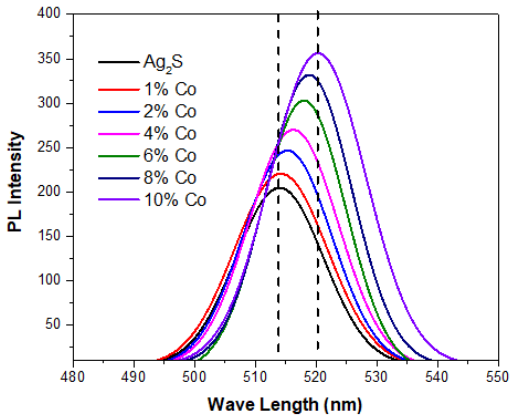

FIG. 9. **PL spectra of Co-doped Ag_2S nanoparticles.**

The normalized PL spectra of Ag_2S doped with Cadmium and cobalt concentrations of 0%, 1%, 2%, 4%, 6%, 8% and 10% are shown in **FIG. 10 and 11**. Clearly, the observed emission band is red-shifted with the addition of Cd and Co. From TEM observations it is seen that the particle size is increased at higher dopant percentages which confirm the redshift at these concentrations of the Cd and Co dopant. This redshift of the emission peak is due to the quantum confinement effect of the nanocrystals.

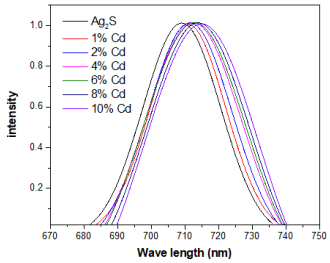

FIG. 10. **Normalized PL spectra of Cd-doped Ag_2S nanoparticles.**

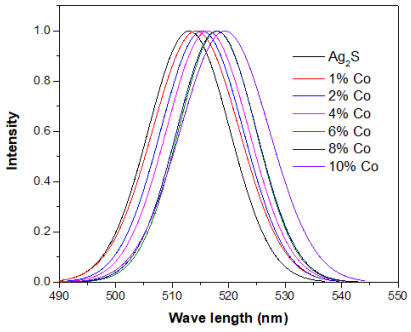

FIG. 11. **Normalized PL spectra of Co-doped Ag_2S nanoparticles.**

Conclusions

Cd and Co-doped Ag_2S have been successfully synthesized by a wet chemical method. The TEM results show that the products were a spherical shape with a size of about 6-15 nm for all Cd and Co-doped Ag_2S nanoparticles. A red shift

phenomenon was found to increase directly with the concentration of Cd and Co doped on to the Ag_2S; this effect has been observed in the UV-vis spectra and Pl spectra of Cd-doped $Ag_2S$and Co-doped Ag_2S samples. With an increasing concentration of Cd incorporated in the nanoparticles, the Cd emission intensity decreases while the intensity of red emission of Co increases. A novel PL phenomenon can be observed from the Ag_2S nanoparticles doped with Cd^{2+} and Co^{2+} ions. This result shows the important roles of dopants in changing the emission color from Ag_2S nanoparticles. Therefore, the size calculated using the Brus equation is closer to values obtained from TEM when the size of particles increases due to the quantum size confinement.

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