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Facile synthesis and antimicrobial activity of CdS-Ag_2S nanocomposites

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ABSTRACT

In this study CdS-Ag_2S nanocomposites for antibacterial activity were synthesized via facile co-precipitation method using PVP as capping agent. The prepared nanocomposites have particle sizes in the range of 50–100 nm (SEM) and PVP addition has good influence on the morphology of nanocomposites. The antimicrobial activity of pure Ag_2S, CdS and CdS-Ag_2S composites was evaluated against *Pseudomonas aeruginosa*, *Staphylococcus aureus* and *Escherichia coli*. The results demonstrate that antibacterial activity was significantly improved due to increasing ratio of CdS into CdS-Ag_2S nanocomposites in comparison to pure Ag_2S and CdS.

1. Introduction

Nanomaterials exhibit superior, unique and indispensable properties and thus have attracted much attention for their distinctive characteristics which were not performed by conventional macroscopic materials [1]. In recent years, the development of efficient chemical and green routes for semiconductor and metal nanoparticle's synthesis has gained significant interest in a variety of areas of nanotechnology [2]. Nanomaterials especially semiconductor based nanomaterials are playing an important role in the progress of nanotechnology due to dynamic role in technological applications and fundamental studies [3]. These semiconductor materials are potential candidates for magneto-optic properties [4], the mineralization of toxic organic compounds [5] and bacteria disinfection [6] etc. Most of the excellent photocatalyst such as metallic sulfide have been extensively utilized in the purification of environment due to their antibacterial behavior [7,8]. The uncontrolled and rapid growth of microorganisms can show the way to serious problems. The development of nanotechnology over the last decade has given us golden opportunities to determine the antibacterial effects of metallic nanoparticles. In addition to the inhibition effect of the particle, metallic nanoparticles have an antibacterial effect, due to their large surface area, small size and large outer surface area. So, the nanoparticles can be used as appropriate alternative to used bio-chemicals [9].

Other than simple nanoparticles, the composites of metal sulfides have shown greater antibacterial activity as compared to simple nanoparticles. T. K. Jana et al. synthesized the CdS/ZnO nanocomposites by using a wet chemical method and tested these nanocomposites against Escherichia coli, Staphylococcus aureus and Klebsiella pneumonia and reported that the antibacterial activity has been enhanced after making composite of ZnO with CdS [10]. Similarly Peng Gao et. al have reported spindle like TiO_2/CdS nanocomposites by using hydrothermal method and has shown that these composites have effectively kill 99% of Escherichia coli in 10 min under visible-light irradiation so resulting in high efficiency than pure TiO_2 and CdS [11]. So these reports have motivated us to make nanocomposites for the optimization of Ag_2S for antibacterial activity.

Silver-based solids/compounds are good antibacterial materials and this activity is due to their high cyto-toxicity against micro-organisms and wonderful broad spectrum antimicrobial activity against many bacteria, such as *E. coli* [12]. Recently the Ag/Ag_2S/rGO has shown excellent antibacterial activity against *Escherichia coli* [13]. Recently reported literature revealed that Ag/Ag_2S nanohybrids and Ag_2S nanostructures have shown enhanced and tunable photo-catalytic and antibacterial properties [14,15]. In other reports, Ag_2S/Bi_2S_3 and F-MWCNTs-Ag_2S based composites demonstrated outstanding antibacterial activity [16,17].

Moreover, Ag_2S is an important metal chalcogenide semiconductor material having narrow band-gap (~1.0 eV). It was widely used in the field of photocatalysis i.e., photocatalytic degradation of organic pollutants [18] and photocatalytic hydrogen production [19] due to its excellent chemical stability and optical properties [20]. Ag_2S has three polymorphic phases monoclinic α-Ag_2S (stable upto 178 °C), body centered cubic β-Ag_2S (stable between 178 °C and 600 °C) and face-centered cubic γ-Ag_2S (above 600 °C). In addition to photocatalysis, the Ag_2S has also been used as fluorescent labels for micro-organisms and biological substances identification. It showed low toxicity and high emission properties [2]. However, there are very few reports about its

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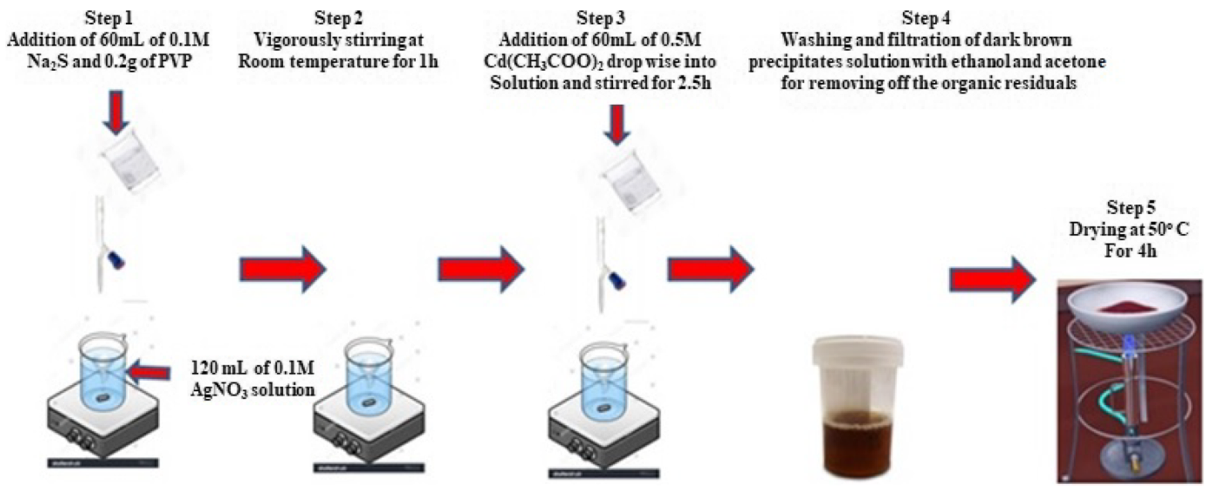

Fig. 1. Schematic diagram of CdS-Ag2S synthesis method.

application as antimicrobial agent. Leila Jafari et al. have shown that rice husk based MCM-41 nanoparticles loaded with silver sulfide nanostructures (Ag_2S/RHA-MCM-41) have shown antibacterial effect against gram negative and positive bacteria [6]. Moreover, like Ag_2S, CdS is also an important II-IV group metal sufide semiconductor having band gap (~2.4 eV). It has vital applications in many fields including optoelectronics, solar cell and the photocatalytic degradation of water pollutants [21]. Especially, it has been extensively used in biological systems, drugs and living organisms. Malarkodi et al. have reported antibacterial activity of CdS nanoparticles against Oral Pathogens [11]. Similarly, Gao et al. have reported that the optimal quantity of CdS kills 99.9% of *Escherichia coli* in 10 min undervisible-light irradiation [22]. The preparation of Ag_2S and CdS has become a very important research area in recent years. Various methods have been used for their preparation: as thermal evaporation [23], ion implantation techniques and sol-gel [24] etc. In all these methods, chemical co-precipitation method is a simple, highly effective, less time consuming and inexpensive aiming highly crystalline nanoparticles technique to obtain Ag_2S and CdS nanoparticles. In addition to above, the combination of CdS and Ag_2S such as CdS-Ag_2S composite has also been reported by some researchers for biological applications [16,25]. For example, E. Jagadeesh et al. have reported their toxic potential against alga *Mougeotia sp* and B. Jayanta et al. have studied the antibacterial activity of mix CdS and ZnS in water treatment [14].

In the present work the facile synthesis of PVP capped CdS-Ag_2S nanocomposites has been reported, which resulted in significantly enhanced structural, morphological and antimicrobial properties. The cadmium sulfide to silver sulfide ratio was varied in order to achieve improved antibacterial activity at an optimum level between two materials. The novelty of this work is that these composites have efficient performance against *Pseudomonas aeruginosa*, *Staphylococcus aureus* and *Escherichia coli*. The results of this work allow us to hypothesize on enhanced antibacterial activity of modified silver sulfide based nanocomposites.

2. Materials and methods

2.1. Reagents

Silver nitrate ($AgNO_3$), sodium sulfide (Na_2S), cadmium acetate (Cd $(CH_3COO)_2$), NaOH, polyvinylpyrrolidone (PVP) with 99% purity (Sigma Aldrich), acetone, ethanol and de-ionized water as washing agent and solvent respectively. Bacterial strains *Escherichia coli* ATCC 25922, *Pseudomonas aeruginosa* ATCC 6749 and *Staphylococcus aureus* ATCC 4163.

2.2. Experimental procedure

The chemical co-precipitation method was used for the synthesis of nanocomposites. In typical synthesis process of CdS-Ag_2S nanocomposites, 60 mL of 0.1 M Na_2S and 0.2 g of PVP was added into 120 mL of 0.1 M $AgNO_3$ solution with vigorously stirring at room temperature for 1 h Then 60 mL of 0.5 M of 60 mL Cd $(CH_3COO)_2$ was added drop wise into the above solution and stirred for 2.5 h. The dark brown precipitates solution was filtered and washed many times with ethanol and acetone for removing off the organic residuals and dried at 50 °C temperature for 4 h. The complete process for the experimentation is shown step wise in Fig. 1.

2.3. Characterizations

The obtained nanocomposites were characterized by using XRD, SEM, FTIR and UV–vis techniques. The X-ray powder diffraction (XRD) spectrum was studied by using X-ray diffractometer (Cu-Kα) source model D8 Advance Bruker Company. Surface morphology of nanocomposites was studied by using scanning electron microscope (SEM). The elemental composition of materials in nanocomposites was studied by using Energy dispersive X-ray spectroscopy (EDX). The adsorption mechanism was studied by FTIR spectra.

2.4. Antimicrobial activity measurement experiment

The antibacterial activity of above mentioned nanocomposites was evaluated by using Well diffusion method. All reagents and glassware were sterilized by an autoclave at 130 °C for 20 min. The pathogenic bacteria Pseudomonas aeruginosa, Staphylococcus aureus and Escherichia coli were used as model test strains. The bacterial cultures in pure form were subculture on nutrient broth medium. With the help of sterile swap each strain was further swabbed equally onto the separate Muller Hinton ager plate. Well of 7 mm diameter was made on Muller Hinton plates using gel puncture. With the help of micropipette, the fixed concentration of 150 μL of Ag_2S, CdS and CdS-Ag_2S nanocomposites solution was poured onto each well on all plates. Incubation was performed at 37 °C for 24 h. The zone of inhibition (ZOI) of each bacterium was measured right after the incubation period.

3. Results and discussion

3.1. X-ray diffraction

The XRD results of pure and modified Ag_2S are shown in Fig. 2. In this Figure, the strong peaks at 33.66°, 37.6° and 46.28° have hkl values

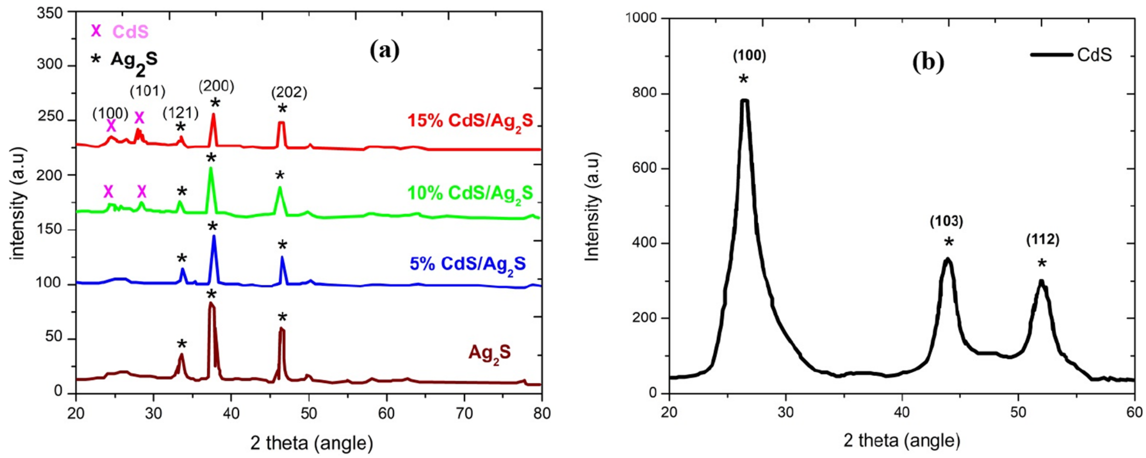

Fig. 2. (a) XRD patterns of different samples of CdS/Ag_2S composites. (b) Pure CdS sample.

as 121, 200 and 202 respectively. These peaks show monoclinic Ag_2S phase and are in agreement with the described data for β–Ag_2S (acanthite) according to (JCPDS 14-0072). Moreover, the XRD patterns of individuals as well as in composite form as CdS-Ag_2S (5%, 10% and 15%) are shown in Fig. 2.

It can be seen that at lower concentration of CdS, there is no peak of CdS but at higher concentration of CdS such as 10% and 15% there are two peaks at 24.9° and 28.3° due to CdS which can be index as (100 and 101) according to (ICDD PDF 80-0006) having hexagonal structure. The results show that the diffraction peaks have been shifted towards higher angles when CdS has been introduced into Ag_2S with high concentration of 10% and 15%. Moreover, the crystallite size was calculated by Scherer equation, the results show that pure Ag_2S has 12.2 nm crystallite size while 5% CdS-AgS, 10% CdS-Ag_2S and 15% CdS-Ag_2S have 11.6, 10.8, and 9.6 nm respectively. This demonstrates that increase in CdS concentration has decreased the crystallite size of CdS-Ag_2S nanocomposite. The decrease in the crystallite size can be attributed to the reason that cadmium may replace silver in silver sulfide crystal due to lower ionic radii (0.97 Å) than silver (1.26 Å) [26].

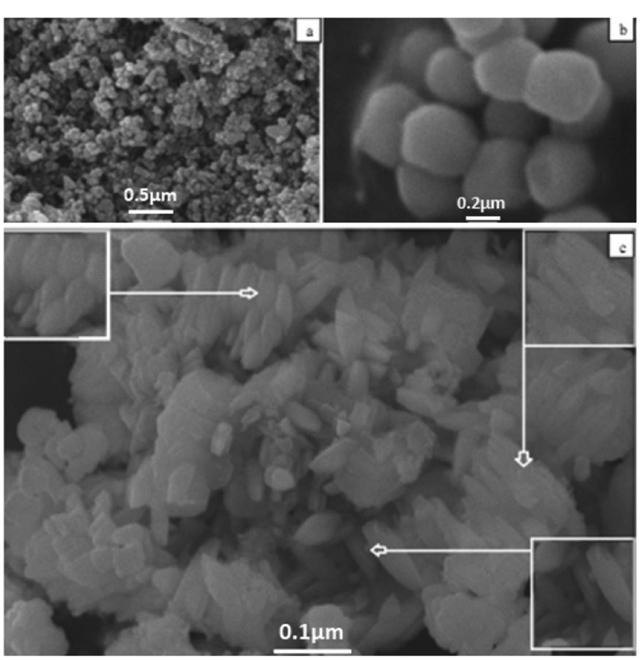

Fig. 3. a,b and c are the SEM Images of 10%CdS-Ag_2S nanocomposites.

3.2. Scanning electron microscopy

The Fig. 3 shows the SEM images of 10% CdS-Ag_2S nanocomposites at different magnification. These images demonstrate that CdS-Ag_2S nanocomposite has spherical shape particles with non-uniform size of 50–100 nm.

The elemental composition of 10% CdS-Ag_2S was measured by Energy Dispersive X-ray (EDX) mode of scanning electron microscope (SEM) and is shown in Fig. 4. The peaks in the EDX result are due to silver (Ag), cadmium (Cd) and sulfur (S) elements. The presence of these elements clearly demonstrates the formation of composite sample.

3.3. FTIR spectroscopy

The FTIR spectra of the prepared nanocomposite were recorded in 500–4000 cm^{-1} range. The spectra are shown in Fig. 5 for pure and modified silver sulfide nanocomposites respectively. The absorption bands at 3580 cm^{-1} to 3620 cm^{-1} is due to free O–H stretching mode of H_2Oimmersed on the surface of nanocomposite. The intense absorption bands in the range of 1030–1060 (sulphate) and 1350–1450 cm^{-1} (sulfoxide) of IR-spectrum shows the presence of S-O group [27]. The peaks in the range 500–750 cm^{-1}can be attributed to metal-sulphur as Ag-S and Cd-S bonds.

3.4. Antimicrobial activity of CdS-Ag_2S based nanocomposites

The antibacterial activity of Ag_2S, CdS and CdS-Ag_2S nanocomposites was observed against *P. aeruinosa*, *E. coli* and *S. aureus* and results are presented in Table 1 along with some previously reported results. The pure Ag_2S has demonstrated bactericidal aptitude of 66 ± 3.2, 80.5 ± 3.2 and 45 ± 1.5 for *P. aeruinosa, E. coli* and *S. aureus* respectively. Under same conditions the bacterial destruction of CdS was 55.1 ± 1.5, 58.7 ± 2.7 and 41.5 ± 1.9 for *P. aeruinosa, E. coli* and *S. aureus* respectively. The minimum inhibitory concentration (MIC) is also shown in Table 2 according to which the MIC value is maximum of 15% composite of Ag_2S with CdS. Hence the antibacterial activity of Ag_2S is higher than CdS. Further the bacterial killing ability was enhanced for CdS-Ag_2S nanocomposites due to increasing addition of CdS as 5%, 10% and then decreased for 15% in Ag_2S and is maximum for 10% addition of CdS as 80.3 ± 2.4, 90.7 ± 2.3 and 53.8 ± 2.3 for *P. aeruinosa, E. coli* and *S. aureus* respectively. The % reduction in micro-organisms was measured by the relation as given below and is shown in Fig. 6.

$$\text{Percentage reduction (\%R)} = (C_c - C_s/C_c) \times 100$$

Where C_c (CFU) is number of bacterial colonies recorded on control and

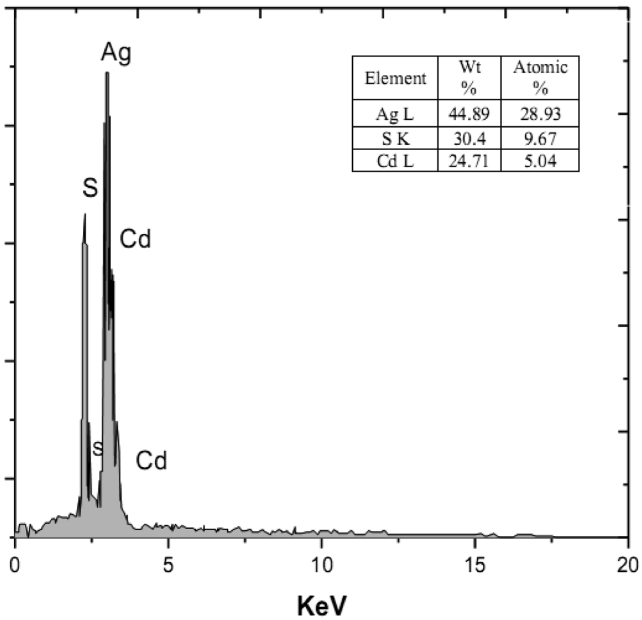

Fig. 4. EDX of 10% CdS/Ag_2S nanoparticles.

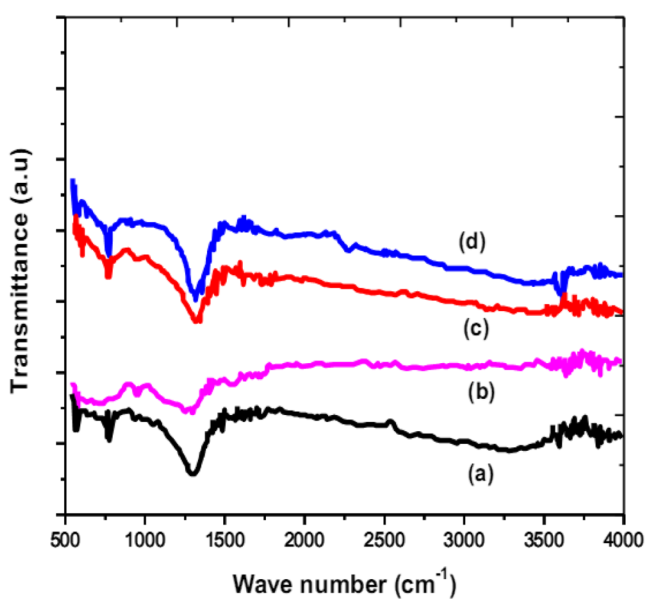

Fig. 5. FTIR spectra of (a) Ag_2S, (b) 5%CdS-Ag_2S, (c) 10%CdS-Ag_2S, (d) 15%CdS-Ag_2S.

Table 1
The antibacterial data for reported literature and this work with Ag_2S, CdS and CdS-Ag_2S nanocomposites.

Sample name	Reduction of Bacteria (%)			References
	P. aeruinosa	*E. coli*	*S. aureus*	
Multiwall CNTs of Ag_2S	78.5 ± 2.9	97.8 ± 2.1	55.7 ± 1.5	[17]
Multiwall CNTs of CdS	68.9 ± 2.5	87.2 ± 4.1	46.7 ± 1.4	
Ag NPs (antimicrobial effect)	7 ppm	259 ppm	[28]	
Ag_2S	66 ± 3.2	80.5 ± 3.2	45 ± 1.5	This work
CdS	55.1 ± 1.5	58.7 ± 2.7	41.5 ± 1.9	
5% CdS-Ag_2S	70.3 ± 2.3	82.3 ± 3.4	46.5 ± 2.7	
10% CdS-Ag_2S	80.3 ± 2.4	90.7 ± 2.3	53.8 ± 2.3	
15% CdS-Ag_2S	74.1 ± 4.2	86.4 ± 1.8	49.6 ± 1.5	

Table 2
The inhibit zone and inhibitory concentration of Ag_2S, CdS and CdS-Ag_2S nanocomposites for *P. aeruinosa*, *E. coli* and *S. aureus*.

Sample name	Bacteria (Inhibition Zone mm)			Minimum inhibitory concentration (MIC) µm		
	P. aeruinosa	*E. coli*	*S. aureus*	*P. aeruinosa*	*E. coli*	*S. aureus*
Ag_2S	25.10	28.10	22.77	69	135	470
CdS	18.34	25.25	20.12	62	120	420
5% CdS-Ag_2S	28.22	30.48	26.44	75	146	520
10% CdS-Ag_2S	35.88	39.24	30.23	87	169	565
15% CdS-Ag_2S	32.90	35.33	28.45	80	155	540

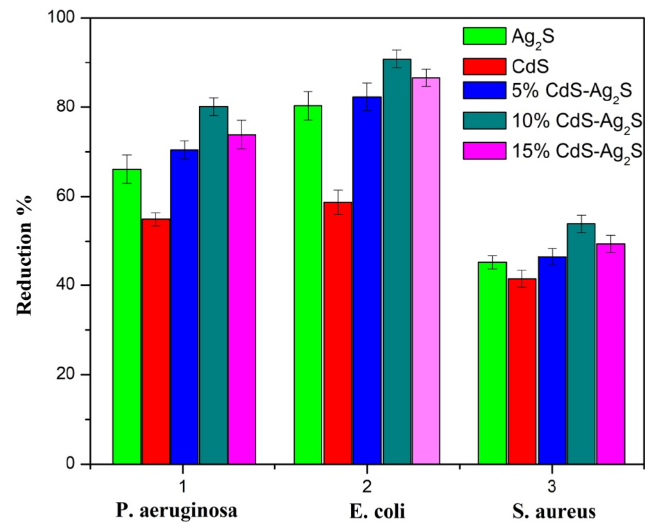

Fig. 6. Antibacterial activity of CdS, Ag_2S and CdS/Ag_2S nanocomposites.

C_s (CFU) is number of bacterial colonies recorded on sample and CFU is colony forming unit.

3.5. Conclusion

In summary, the effect of PVP and CdS has been seen on silver sulfide nanoparticles using the chemical co-precipitation method which is very simple and economical method. The modification in Ag_2S has been made by increasing concentration of cadmium sulfide as 5%, 10%, and 15%. XRD results show that Ag_2S has β–Ag_2S (acanthite) phase with particles size in 50–100 nm range according to SEM images. The antibacterial activity i.e germicidal action of CdS-Ag_2S nanocomposites have shown that these can be successfully used in home appliances, medicines and also in sporting goods.

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