EFFECT OF LA AND SN DOPING ON PHOTOCATALYTIC ACTIVITY OF CADMIUM SULPHIDE PHOTOCATALYST

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ABSTRACT

Cadmium Sulphide photocatalyst doped with La and Sn and pure were prepared by chemical coprecipitation method. The prepared samples were characterised by SEM (Scanning Electron Microscopy), EDX (Energy Dispersive X-Ray Diffraction), XRD (X-Ray diffraction) spectroscopy. Photocatalytic degradation experiment was carried out in UV-Photoreator for degradation study in UV light. The photocatalytic activity of La and Sn doped Cadmium Sulphide was studied by checking the change in initial COD and final COD. La and Sn doped Cadmium Sulphide have good efficiency to degrade the phenolic compound. The doped Cadmium Sulphide has best degradation efficiency in UV light.

***KEYWORDS*:** Photocatalyst, nanoparticles, coprecipitation method.

1. INTRODUCTION

Photocatalysis is the alteration of the rate of reaction by using catalyst in presence of light. The process uses atmospheric oxygen as an oxidant and it can be carried out under ambient conditions using a semiconductor photocatalyst [1]. Now days photocatalytic degradation of various organic compounds is possible using photocatalyst. Metal oxide and metal sulphide semiconductors are considered to be more suitable photocatalysts due to their photocorrosion resistance and wide band gap energies. Earlier researchers have used to study the photocatalytic degradation of organic compounds by using photopcatalysts like CuS, ZnO, ZnS, TiO_2, CdS etc. Photocatalysts are mainly used in waste water treatment.

Cadmium Sulphide is a II-VI group semiconductor having a band gap of 2.42 eV. The band gap of cadmium sulphide can be adjusted by doping it with impurities. Because of particle size and crystalline structure it shows special opto-electrical and chemical properties [2, 3].

Several methods are used to synthesize Cadmium Sulphide nanoparticles like sol-gel method, mechano-chemical method, surface ionic layer adsorption and reaction method (SILAR), microemulsion method, spray

pyrolysis method, chemical bath deposition method and chemical co--precipitation method etc [4,5,6]. In present study, La and Sn doped Cadmium Sulphide nanoparticles were synthesized by co-precipitation method. It is very efficient, having simple route of synthesis and requires less environmental conditions. It consumes less time for the synthesis.

2. EXPERIMENTAL WORK

2.1 SYNTHESIS OF LA AND SN DOPED CDS

Cadmium sulphide nanoparticles doped with Sr and Sn were prepared by chemical co-precipitation method. For the synthesis of CdS nanoparticles, cadmium acetate dihydrate (1 M), Lanthanum nitrate (0.05 M), stannous chloride $SnCl_{.2.}$ $2H_2O$ (0.05M), and sodium sulphide (1M) were used. All the chemicals used were analytical grade. Distilled water was used as solvent.

For the synthesis, calculated amount of all the reactants dissolved in distilled water separately. The mixture of Cadmium acetate, Stannous chloride and lanthanum nitrate was stirred on magnetic stirrer. Sodium sulphide was added drop wise with constant stirring. Ammonia solution was added to maintain the pH~11 [4].

The yellow colour solution was formed. The mixture was then stirred at 70^0 C for about one hour. Yellow colour solution turned to precipitate was filtered, washed with water and acetone several times to remove the organic residue present in the nanoparticles. Then sample was taken to an oven for about 6-8 hours then it was kept in a desiccators before taken to the characterization.

2.2 CHARACTERISATION OF SAMPLE

The samples were characterized to determine the morphology of prepared nanomaterials by SEM, elemental analysis for the confirmation of doping of La and Sn by EDX and crystal structure by XRD.

2.3 PHOTOCATALYTIC DEGRADATION EXPERIMENT

Study of photocatalytic degradation was performed the photocatalytic degradation of 25 ppm phenol solution in visible light and UV-light. For the experiment in Visible light, 200 ml of 25 ppm phenol solution was taken in a beaker and 200 mg of doped and pure Cadmium Sulphide photocatalyst was added to it. The solution was then stirred on magnetic stirrer for about 7 hours. For the study of photocatalytic degradation under UV light 200 ml of 25 ppm phenol solution was taken in reaction flask of UV photoreactor and 200 mg photocatalyst was added to it. This solution was stirred in UV light for about 7 hours. For the conformation of photodegradation of 25 ppm phenol solution, the COD was checked. The initial absorbance and absorbance at one hour time interval were recorded.

3. RESULTS AND DISCUSSION

3.1 SCANNING ELECTRON MICROSCOPY

The morphology and topography of La and Sn doped Cadmium Sulphide nanoparticles were studied by Scanning Electron Microscopy. Figure 1 and 2 shows the SEM images of La and Sn Doped CdS. From the SEM, it is observed that, clusters of nanoparticles are equally distributed. Most of the particles are spherical in shapes. SEM data reveals the particles of doped CdS photocatalyst materials are nano sized. The surface grain size is more than void area which indicates the formation of high quality of the crystals

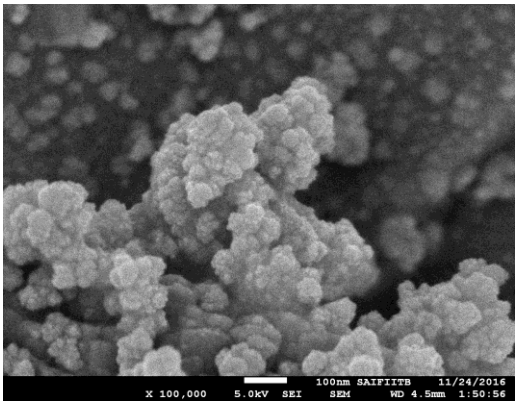

Figure 1 SEM image for La and Sn doped cadmium Sulphide nanoparticles

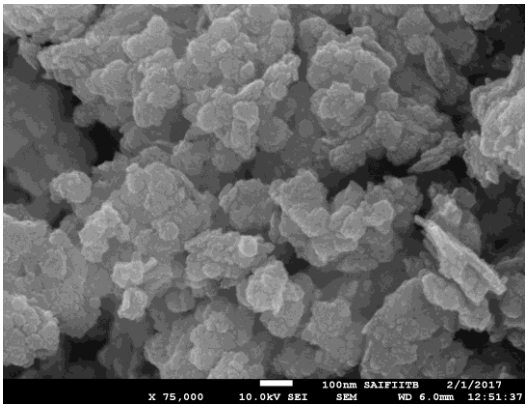

Figure 2 SEM mage for pure Cadmium sulphide nanoparticles

The both high resolution SEM images are showing the sponge like appearance of hexagonal Cadmium Sulphide nanoparticles.

3.2 ENERGY DISPERSIVE X- RAY ANALYSIS

Elemental study of prepared La and Sn doped Cadmium Sulphide and pure Cadmium Sulphide is carried out with the EDX. Figure 2.3 is representing the EDX spectra of La and Sn doped Cadmium Sulphide and pure Cadmium Sulphide.

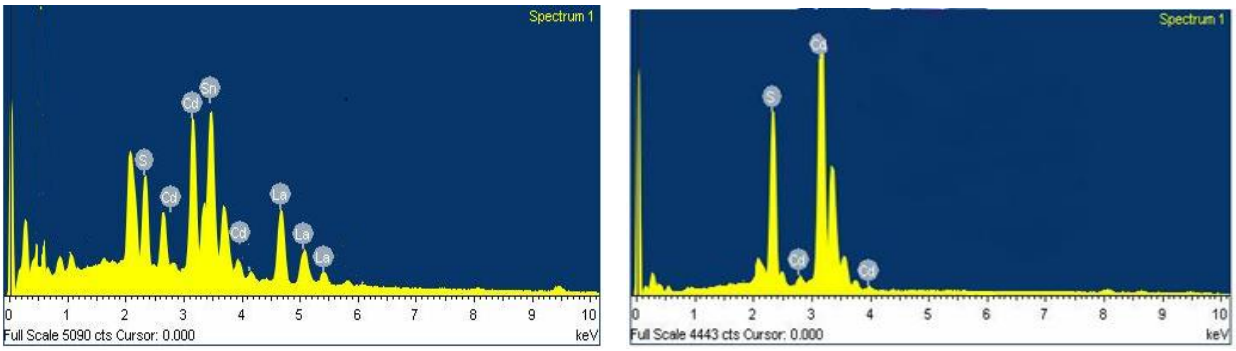

Figure 3 EDX image of a. La and Sn doped CdS b. Pure CdS

In above spectra image a. shows shows the peaks for La and Sn is successfully incorporated in Cadmium Sulphide Crystals. Image b. is showing the clear peaks for Cd and S.

3.3. X-RAY DIFFRACTION TECHNIQUE

Crystal structure study was done by X-Ray diffraction study. Figure 4 is showing the XRD data for La and Sn doped CdS. With XRD data the particle size of the pure and doped Cadmium Sulphide nanoparticles was calculated by using the Sherrer equation

$$d = \frac{K\lambda}{\beta \cos\theta}$$

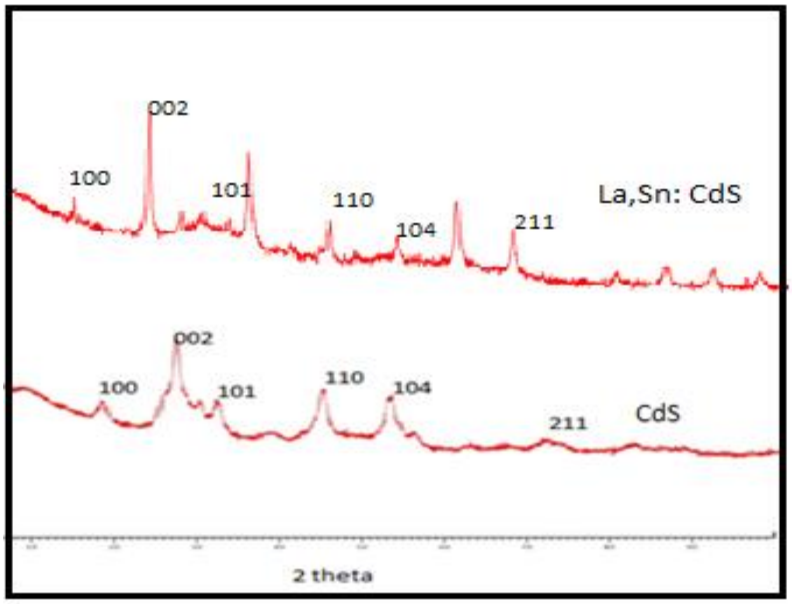

Figure 4 XRD pattern of La and Sn doped CdS and pure CdS nanoparticles

The fig. 4 data reveals that 100, 002, 101, 110, 104, 211 are the XRD planes for hexagonal Cadmium sulphide. The narrow intense peak indicated the high crystallinity of the nanoparticles. The calculated particle size for La and Sn doped Cadmium Sulphide and pure cadmium Sulphide is 67.77nm and 84 nm respectively. The XRD data thus reveals the particle size of Cadmium Sulphide nanoparticles decreases on doping with La and Sn.

3.4 UV-VISIBLE SPECTROSCOPY

Optical properties of prepared La and Sn doped Cadmium Sulphide and pure Cadmium Sulphide were studied by UV- Visible spectroscopy. The UV-Visible spectra of prepared nanoparticle was recorded on Hatch DR 5000 spectrophotometer. The wavelength maximum was recorded on spectrophotometer and the band gap of doped and undoped Cadmium Sulphide was calculated as in table 1.

Samples	λ_{max} nm	Band gap eV
$La_{0.05}$ $Sn_{0.05}$ CdS	545	2.27
CdS	501	2.47

Table 1. Band gap of La and Sn doped Cadmium Sulphide and pure Cadmium Sulphide

The optical band gap of La and Sn doped Cadmium Sulphide prepared by coprecipitation method was found to be 2.47eV which was tuned by doping the Cadmium Sulphide By Lanthanum and Tin.

3.4 Photocatalytic Activity

Sn and Sr doped Cadmium Sulphide shows good degradation in both visible and UV light. Photocatalytic activity of pure and La and Sn doped photocatalyst was studied in presence of UV and Visible light.

a. In Solar light

For the solar light photodegrdation experiment 100 ml of 20 ppm phenol was taken in 250ml beaker, 100ml of catalyst was added to it and it was stirred in solar light for six hours. After each one hour phenol sample was taken out and its COD was determined. The graph shows decrease in COD, against time in Fig. 4.

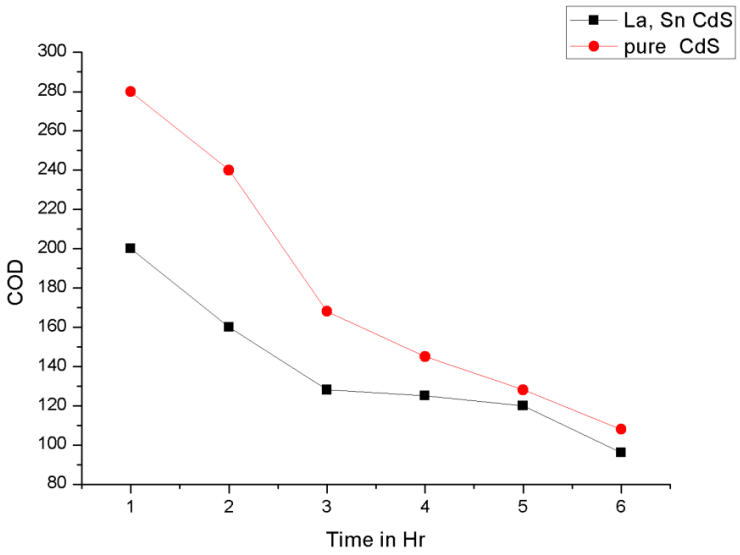

Figure 4 Photodegradation of 20 ppm phenol in Solar light

The calculated initial COD of 20 ppm phenol was 360 and it was gradually decrease by loading both pure and La and Sn doped CdS. It is clear from graph that the La and Sn doped Cadmium Sulphide have good tendency to degrade the phenol than the pure Cadmium Sulphide nanoparticles. The decrease in band gap as well as decrease in particle size of prepared nanoparticles is major reason behind it.

b. In UV Light

For the Photodegradation in Ultra –Violet light 100ml of 20ppm phenol solution was taken in reaction flask of UV photoreactor. 100 mg of Cadmium Sulphide photocatalyst was added to it. It was stirred under UV lamp of 13 watt for about six hours. For checking the COD at every hour time interval, the samples were withdrawn at each hour and its COD was measured. Same procedure was followed for La and Sn doped Cadmium Sulphide nanoparticles. The decrease is COD of phenol has been seen in both the pure and La and Sn doped Cadmium Sulphide nanoparticles. Then COD was plotted against time is shown in figure 5.

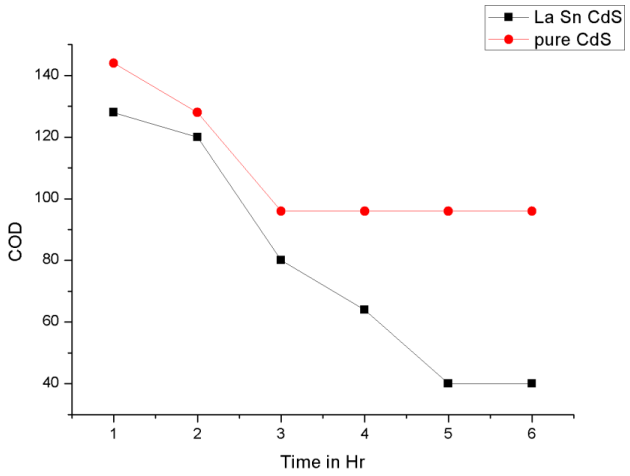

Figure 5 Photodegradation of 20ppm phenol in UV light

It is clear from graph La and Sn doped Cadmium Sulphide shows greater degradation than of phenol than pure Cadmium Sulphide in UV light. The initial COD of phenol was 360ppm which was reduced to 40 ppm by using La and Sn doped Cadmium Sulphide and 96 ppm by pure Cadmium Sulphide. This is due to the decrease in size of nanoparticles provides the large surface area for the photocatalytic reaction. The minimisation of band gap also fascinates the highest degradation rate in UV-light.

4. CONCLUSIONS

The yellow coloured precipitate of La and Sn doped Cadmium Sulphide and pure Cadmium Sulphide nanoparticles prepared by Chemical Coprecipitation method were highly crystalline. On doping with La and Sn particle size of Cadmium sulphide nanoparticles were decreased. The decrease in size of nanoparticles and decrease in band gap shows increase photocatalytic activity of La and Sn doped Cadmium Sulphide than pure Cadmium Sulphide. Pure and doped Cadmium Sulphide has greater photocatalytic activity in UV light as compared to solar light.

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5. ACKNOWLEDGEMENT

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