



Effect of Indium doping on the photoelectrochemical and photocatalytic properties of zinc sulphide



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ABSTRACT

In this article, the visible light enhanced photoelectrochemical and photocatalytic properties for nano-sized Indium doped Zinc Sulphide compared to undoped ZnS had been reported. Both ZnS and In doped ZnS (In-ZnS) were synthesized through soft chemical route by a co-precipitation method. ZnS and In doped ZnS existed as single phase having cubic structure. These samples were nano-sized with a particle size of approximately 24 nm. SEM images revealed the presence of aggregated particles with a wide distribution in the particle size. UV–visible Diffused Reflectance Spectra showed improved visible light absorption for the doped sample as compared to the undoped sample. X-ray photoelectron studies indicated the presence of indium as In³⁺ in In-ZnS. Photoluminescence studies suggested the presence of both zinc and sulfur vacancies in these samples. After the doping of ZnS with In, there was an increase in photocurrent under visible light irradiation. The doped sample also exhibited enhanced photocatalytic activity for hydrogen generation. A good correlation between photocatalytic and photoelectrochemical properties was seen for both ZnS and In doped ZnS. The improvement in In doped ZnS has been attributed to the increased visible light absorption arising due to the decreased band gap of the doped sample.

1. Introduction

The primary source of energy is fossil fuels at present. Fossil fuels are not just the energy source but also a raw material for the synthesis of many chemicals and materials. The increase in the global temperature i.e. global warming and environmental pollution in the form of air pollution, water pollution etc. is some of the impacts of fossil fuels on the environment, which is visible all across the globe. Apart from the obvious degradation to the environment, fossil fuel is a non renewable resource.

Currently attention is focused on the utilization of solar energy to meet our rising energy demands. It can be done in two ways, either in the form of solar cells for the production of electricity from photo-sensitive semiconductor materials [1]. Or it can be used for the generation of fuels like hydrogen from water using either as a semiconductor photocatalyst or as a photoelectrode. Solar cells have found its way into the energy sector by using silicon, but now the attention is focused on semiconductor materials like Copper Indium Selenide, Copper Zinc Tin Selenide and Copper Indium Gallium Selenide [1,2]. These semiconductors are being used as absorber layers with solar cell efficiency less than 10%. If the efficiency of these cells can be improved

at a lower cost, then it can find applications at a greater scale. As part of the efforts in developing renewable energy based fuels, hydrogen has gained importance in the last few decades. Hydrogen when burned produces water and hence produces no harmful products and by-products after combustion. If it can be manufactured from a renewable source of energy then it can be a greener fuel compared to the fuels in use today. Studies are being done for the production of hydrogen from water, using photocatalyst/ photoelectrode and solar energy [3]. Efforts are being focused at present onto making semiconductors active in the visible region, since 45% of the solar radiation falls in visible region [4]. Semiconductor materials such as CdS, CdSe etc. have suitable band gaps, which enable them to be active under visible light. But, these chalcogenides undergo photocorrosion and they are not environment friendly, which demand the need for better, viable alternatives [5]. ZnS is another wide band gap material that can be useful in the development of a photocatalyst as well as a photoelectrode [6–8]. Many dopants are used for decreasing the bandgap and improving the optical absorption properties of ZnS. Doping of ZnS with materials like Ni, Cu, Cd etc. has resulted in a decrease in band-gap and increase in the photoactivity [9–13].

Indium doped ZnS thin films have been studied for the possible

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applications of optoelectronic devices. It was reported that optical property and electrical conductivity of In doped ZnS is higher than undoped ZnS [14]. Cu and In co-doped ZnS was reported to exhibit enhanced photocatalytic activity for hydrogen generation than ZnS, which was attributed to the increased visible light absorption [15]. It was shown that Ag and In co-doping improved the photocatalytic performance of ZnS due to the improved optical absorption properties and better separation of charge carriers brought about by Ag [16]. In and Ag doped ZnS with Ru as co-catalysts was found to be an efficient catalyst for hydrogen generation from water [17]. The enhancement was attributed to the efficient separation of charge carriers due to the presence of Ru co-catalyst.

The main aim of the present work was to assess the effect of doping indium in ZnS on the photoelectrochemical and photocatalytic properties. Though the photocatalytic activity and electrical conductivity of In doped ZnS had been reported, no attempt was made to study the photoelectrochemical property and correlate it with its photocatalytic activity. In this study, the photocatalytic and photoelectrochemical properties of the indium doped and undoped ZnS samples had been investigated and a comparison was made between these properties.

2. Materials and methods

2.1. Synthesis

Precursors used for the synthesis such as zinc acetate (Loba Chemie, Mumbai, India), indium chloride (Sigma Aldrich, St. Louis, USA) and sodium sulphide (S.D. Chemicals, Mumbai, India) were used as received. For the preparation of 2% Indium doped Zinc Sulphide ($Zn_{0.98}In_{0.02}S$, referred in the text as In-ZnS) 2.685 g of Zinc acetate was mixed with 20 ml of ethanol and 20 ml water. 0.06 g of Indium Chloride was added to 5 ml ethanol and 5 ml water. 3 g of Sodium Sulphide was dissolved in a mixture of 20 ml of ethanol and 20 ml water. This was followed by the addition of sodium sulphide solution, drop by drop to the mixed solution of zinc acetate and indium chloride, under constant stirring. After precipitation, the stirring was continued for two hours. The product was then centrifuged and washed with ethanol and water, three times each. After drying, the compound was heated in a tubular furnace, in Argon atmosphere at 350 °C for four hours. Zinc Sulphide was prepared by the precipitation of zinc acetate using sodium sulphide, and a similar procedure was used. Photoelectrodes were prepared by spin casting ZnS and In-ZnS on p-type Silicon with low resistivity ($\rho = 1-10 \Omega\text{-cm}$).

2.2. Characterization

A Philips PW1820 X-ray Diffractometer attached with a PW 1729 generator was used to record the X-ray diffraction (XRD) patterns of these powder samples. The machine was operated at 30 kV and 20 mA. Graphite crystal monochromator was used so that monochromatic $CuK\alpha$ radiation is obtained. The SEM micrographs of powder samples prepared were recorded using SEM machine, Seron Technology Inc. Korea, (Model No. AIS2100). UV-visible diffused reflectance spectra (UV-vis DRS) were recorded in a Jasco (model V-670) spectrophotometer having an integrating sphere accessory. The reference used was Barium sulfate for recording the reflectance spectra. X-ray photoelectron spectra (XPS) were recorded in a VG Microtech electron spectrometer using $MgK\alpha$ X-rays ($h\nu = 1253.6 \text{ eV}$). The chamber pressure was maintained at 1×10^{-9} Torr. Peak positions were corrected using the C 1s signal present at 284.5 eV. XPS Peaks were deconvoluted using XPS 4.1 software, which used a combination of Gaussian and Lorentzian functions after subtracting the background by the Shirley method. Photoluminescence (PL) spectra were recorded using Edinburgh Instruments FLSP 920 and 450 W Xe arc lamp was used for the excitation of samples. A Hamamatsu R2658 PMT, which was cooled by Peltier element, was used as the detector. Emission

patterns were corrected for the detector response and were measured at 1 nm resolution.

2.3. Photocatalytic activity measurement

The photocatalytic activity was studied for ZnS and In-ZnS using the following procedure. The reaction was carried out in a glass reactor which was irradiated using visible light. The experimental setup consisted of an irradiation chamber for irradiating the samples and a gas chromatograph for analyzing the products to determine the quantity of hydrogen produced. The reactor was provided with a side tube which was closed with a silicone rubber septum. 0.05 g of catalyst was added to the reactor along with 12.5 ml of 0.6 M Na_2S and 12.5 ml of 0.8 M Na_2SO_3 . Na_2S and Na_2SO_3 acted as sacrificial reagents, for hole scavenging. The reactor was flushed with Argon gas before irradiation. It was irradiated in a circular chamber of internal diameter 44 cm and height of 46 cm, fixed with eight ordinary fluorescent lamps (Wipro Fluorescent lamp) (36 watts each) symmetrically on the walls. The radiation produced by the lamps was mainly in the visible light region ($UV < 3\%$). After every hour, the gas mixture in the reactor was analyzed using a gas chromatograph (Chromatography and Instruments Company, Gas Chromatograph GC2011). It contained a molecular sieve 5 A column and used a thermal conductivity detector.

2.4. Photoelectrochemical experiment

Photoelectrode was fabricated by using spin coating method (Programmable Spin Coater, Model No. SCU-2008 C, Apex Instruments Co.). 0.022 g of ZnS/In-ZnS was dispersed onto 1 ml methanol. The vial was then sonicated and left to settle the bigger particles. A drop of the supernatant solution was then placed on the Si substrate and the spin coating program was started. The procedure was repeated to get a thin uniform coating on Si, keeping all the parameters same for both samples. The films were then heated at 60 °C for one hour. The photoelectrochemical cell (PEC) consisted of ZnS/In-ZnS coated on Si (p-type, (1 1 1) orientation, $\rho = 1-10 \Omega\text{-cm}$) as the working electrode, platinum mesh as the counter electrode and platinum wire as a pseudo reference electrode. Here, silicon with resistance of the order of 1–10 $\Omega\text{-cm}$ is used as a conducting substrate for depositing ZnS/In-ZnS. The electrolyte used was 0.1 N Na_2SO_4 . The electrochemical cell was connected to the potentiostat to study the current-voltage (I-V) characteristics under light and dark condition, and to perform chronoamperometric switching studies. Cell was irradiated using a fluorescent lamp and the light intensity incident on the samples was 200 $\mu\text{W}/\text{cm}^2$. The radiation from fluorescent lamp consisted of mainly visible light having a small amount of UV ($UV < 3\%$).

3. Results and discussion

3.1. XRD, Raman and morphological studies

Fig. 1 shows the XRD patterns of ZnS and In-ZnS. The patterns showed that ZnS existed in cubic phase (PC PDF Card No. 80-0020). The XRD pattern showed peaks corresponding to 2θ values of 28.6, 48.0 and 56.9° corresponding to the reflections from crystal planes of (1 1 1), (2 2 0) and (3 1 1) respectively. The pattern indicated that the doped sample existed as single phase and no second phase of indium sulphide or oxide was seen. Scherrer equation was used to determine the crystallite size of ZnS and In-ZnS. The crystallite size, calculated from the width of the (1 1 1) peak, are 26 nm and 22 nm for ZnS and In-ZnS respectively.

To further ascertain whether any other phases are present in these catalysts, Raman spectra were recorded. Fig. 2 shows the Raman spectra of ZnS and In-ZnS. Raman bands present at 208 cm^{-1} could be assigned to the first order longitudinal acoustic (LA) mode of ZnS [18]. The bands at 278 and 348 cm^{-1} were assigned to longitudinal optical

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