



Microflowers of Pd doped ZnS for visible light photocatalytic and photoelectrochemical applications

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ABSTRACT

A new modification of zinc sulfide, which is microflowers of Pd doped ZnS, is investigated as photocatalyst for hydrogen generation from water. Pd doped ZnS shows significant photocatalytic activity when irradiated with visible light compared to ZnS. Both ZnS and Pd doped ZnS exist as cubic phase and in Pd doped ZnS, Pd substitutes Zn in the ZnS lattice. A change in the morphology of ZnS from irregular shape to rose flower like structure and increased surface area are observed after Pd doping. Increased visible light absorption and a red shift in the absorption edge is observed for the doped ZnS. Photoluminescence spectra suggest the presence of defect energy levels/surface states within the bandgap of ZnS due to the zinc and sulfide ion vacancies. Palladium exists as Pd²⁺ in doped ZnS and formation of metallic Pd does not occur after photocatalysis experiment. Photocatalytic activity of Pd doped ZnS shows the trend: 5%Pd-ZnS > 3%Pd-ZnS > 2%-Pd-ZnS > 6% Pd-ZnS > ZnS. The catalyst is stable for repeated use up to 60 h. Photoelectrochemical studies show enhanced photocurrent for the doped ZnS, which is in conformity with its photocatalytic property. These improved properties of the Pd doped ZnS is ascribed to the increased visible light absorption and to the increased surface area.

1. Introduction

Visible light active semiconductors are attractive candidates for photocatalytic applications as solar radiation constitutes around 43% visible light. Most of the efficient photocatalysts developed so far are active only in the ultra violet (UV) light, which limits its capacity for solar energy utilization as the UV light content in solar radiation is 3–5%. Semiconductor materials such as CdS, CdSe, CdTe have narrow band gaps due to which they can absorb visible light and carry out photocatalytic reactions [1]. But, these chalcogenides are not environment friendly and can undergo photocorrosion. ZnS is another chalcogenide, which is relatively less toxic and can be used as a photocatalyst as well as a photo electrode. Another important advantage of ZnS is that it has higher negative conduction band potential due to which it can efficiently reduce water to generate hydrogen [2]. However, ZnS is a wide bandgap material (bandgap = 3.6 eV) and requires UV light for its excitation.

Several efforts are made to decrease the bandgap of ZnS using different dopants like Cu, In, Ni, Cd etc. By doping ZnS with these elements, the band structure can be modified and can enhance the visible light photocatalytic activity [3–8]. Cd has been used very widely to

dope ZnS as a large concentration of Cd can be doped into ZnS without the formation of a second phase. Besides, by varying the concentration of Cd, the bandgap can be tuned so that it can extend the absorption of light from UV to visible region [9–12]. It is reported that by varying the Cd concentration in ZnS from 0.2 to 0.8, the bandgap of ZnS decreases from 2.87 to 2.33 eV respectively and the highest photocatalytic activity is exhibited by a solid solution of composition, Zn_{0.5}Cd_{0.5}S [13]. In another study, a gradual red shift in the absorption edge of ZnS is reported as the concentration of Cd is varied from 0.19 to 0.8 and the highest photocatalytic activity for hydrogen generation is obtained for Zn_{0.81}Cd_{0.19}S [14]. The band structure of Zn_{1-x}Cd_xS solid solution is found to depend on the concentration of Zn and a higher photocatalytic activity is obtained when 'x' is varied from 0.2 to 0.3 in this study [15]. The increased activity is attributed to the altered level of conduction band and improved optical absorption property of the solid solution. Co-doping of ZnS with Cu and Cd results in a red shift of the absorption edge to 560 nm and shows enhanced photocatalytic activity compared to Cd doped ZnS and undoped ZnS due to the increased visible light absorption of the new compound [16].

Though Cd doped ZnS is an efficient photocatalyst for water splitting reaction, an alternative dopant to Cd is to be explored to make it

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non-toxic and environment friendly. Other dopants employed for this purpose are In, Ni and Cu. Doping ZnS with In results in enhanced photocatalytic activity due to the increased visible light absorption resulting from the modification of the band structure of ZnS as a result of In doping [5]. ZnS doped with Ni shows enhanced photocatalytic activity for dye degradation due to factors such as the alteration of bandgap, phase change from cubic to wurtzite and change of semiconductor type from 'n' to 'p' [4]. It is reported that a 'shell' type Cu doped ZnS shows higher photocatalytic activity for hydrogen generation from water compared to un-doped ZnS. This is attributed to the extended optical absorption beyond 440 nm [8].

The aim of this study is to partially substitute ZnS with Pd so that its optical properties can be enhanced. As the ionic radii of 4 coordinated Pd^{2+} (0.64 Å) and Zn^{2+} (0.60 Å) are comparable [17], it is expected that Pd^{2+} can substitute Zn^{2+} in the ZnS lattice. Effect of modification of the band structure of ZnS by Pd on its photocatalytic and photoelectrochemical properties has not been reported so far. This modified compound is expected to have decreased bandgap, increased visible light absorption and similar photocatalytic and photoelectrochemical properties. A detailed physico-chemical characterization of the compound is done and an attempt is made to correlate these properties with the observed photocatalytic and photoelectrochemical behavior.

2. Experimental

2.1. Synthesis

Zinc acetate, Palladium chloride and sodium sulfide were used as received for the synthesis of ZnS and Pd doped ZnS. A series of Palladium doped ZnS (2%, 3%, 5%, and 6% by atomic weight) were synthesized by co-precipitation method. The following procedure was used for the preparation of palladium doped Zinc Sulfide (referred in the text as xPd-ZnS, where 'x' is the concentration of Pd in ZnS). Zinc acetate and sodium sulfide were dissolved in a mixture of 20 ml of ethanol and 20 ml water separately. Required amount of palladium chloride was added to 5 ml ethanol and 5 ml water. Sodium Sulfide solution was added slowly to the mixed solution of zinc acetate and palladium chloride, under constant stirring. The suspension was stirred for two hours. The product was then centrifuged and washed with water and ethanol. After drying, the photocatalysts were calcined at 350 °C in air for four hours. Zinc sulfide was prepared by the same method by the precipitation of zinc acetate by adding sodium sulfide.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns were recorded in a Philips PW1820 x-ray diffractometer having a PW 1729 generator. Current applied was 20 mA and a voltage of 30 kV was applied. To record XRD patterns, monochromatic CuK_α radiation was used. Scanning electron micrograph (SEM) images of the samples were recorded using the Seron SEM machine (Model No. AIS2100). Surface area measurements were done by Brunauer-Emmet-Teller (BET) method. The instrument used was Micromeritics ASAP 2020 V3.04H and nitrogen was used as adsorbate at 77 K. Pore size distribution of Pd doped ZnS was found out by the Barret-Joyner-Halenda (BJH) method. A procedure of degassing the samples at 300 °C for 2 h was done before the measurements. UV-visible diffused reflectance spectra (UV-vis DRS) were recorded in a Jasco spectrophotometer (model V-670) containing integrating sphere accessory. The reference used was Barium sulfate. Edinburgh Instrument (FLSP 920 system) combined with 450 W Xe arc lamp and Hamamatsu R2658 PMT detector was used for recording photoluminescence spectra. The excitation wavelength used was 282 nm and the spectra were corrected for the detector response. The measurements were done at 1 nm resolution. The oxidation states of the different elements present in the system were determined using X-Ray Photoelectron Spectroscopy (XPS). A VG Microtech electron

spectrometer was employed for this purpose and the energy of the Mg K α X-rays used was 1253.6 eV. The chamber pressure was kept at 1×10^{-9} Torr. Correction of the peak positions were done using the C 1s signal appearing at 284.5 eV. Deconvolution of the spectra was done using XPS 4.1 software. In this fitting procedure, a combination of Gaussian and Lorentzian functions is applied and the background is subtracted by the Shirley method.

2.3. Photocatalytic experiments

Photocatalytic activity measurements were done using three different light sources.

One set of experiments were conducted using day-light fluorescent lamps as light source and a tubular glass (Pyrex) reactor was used for this experiment. Details of the reactor, irradiation chamber and emission profile of the fluorescent lamp are given in our earlier articles [18–20]. Photocatalytic experiments were conducted under the following conditions. Fifty milligram of catalyst was suspended in a mixture of 12.5 ml Na_2S (0.6 M) and 12.5 ml Na_2SO_3 (0.8 M) aqueous solutions. The suspension was stirred using a magnetic stirrer and irradiation was done from all sides. The light flux incident on the reactor was measured using a calibrated energy meter (Gentec Solo2) and the value obtained was 10 mW/cm².

To find out the visible light photocatalytic activity, Xenon arc lamp was used as light source. For this, 50 mg of catalyst was suspended in 14 ml of Na_2S and Na_2SO_3 solutions (7 ml each) and the experiment was done under constant stirring. The suspension was illuminated on one side using a collimated beam of 1 in. diameter (Irradiated area is $\sim 5 \text{ cm}^2$). A cut-off filter ($> 410 \text{ nm}$) was used to obtain only visible light. Light intensity incident on the reactor was 180 mW/cm².

To determine the photocatalytic activity under solar light, a solar simulator was used. A cylindrical reactor containing 80 mg catalyst suspended in a mixture of 40 ml of Na_2S + 40 ml Na_2SO_3 was irradiated from the top (irradiated area 50 cm², light intensity = 100 mW/cm²) under constant stirring.

All experiments were done under argon atmosphere. The amount of hydrogen in the mixture was determined hourly using a gas chromatograph (Chromatography and Instruments Company, GC 2011) fitted with a molecular sieve 5A column and a thermal conductivity detector.

Details of apparent quantum efficiency calculation are given in our earlier publications [18–20]. Solar to hydrogen energy conversion efficiency was determined using the equation [21].

$$\eta\% = \frac{\text{H}_2(\text{moles/s}) \times \Delta G^0(\text{H}_2\text{O})(\text{J/mole})}{\text{Incident energy}(\text{watt/cm}^2) \times \text{irradiated area}(\text{cm}^2)}$$

where ΔG^0 is the standard Gibbs free energy of water.

2.4. Photoelectrochemical experiment

For making photoelectrodes, ZnS and 5Pd-ZnS samples were spread evenly on silicon substrate (p-type, (100) silicon, $\rho = 1-10 \Omega\text{-cm}$) and dried it at 60 °C in air. The area of the electrochemical cell is 0.385 cm². In this case, the combination of p-type silicon and n-type ZnS can end up in a p-n junction. But, as the silicon used has a resistance of $\sim 1-10 \Omega\text{-cm}$, it can be considered as a conducting substrate and not a p-type semiconductor. In the present photoelectrochemical cell, Si/ZnS or Si/5Pd-ZnS was the working electrode, Pt was the counter electrode and Pt wire was the pseudo reference electrode. The electrolyte used was a mixture of Na_2S + Na_2SO_3 (1:2) aqueous solution. Potentiostat 2273 was used for electrochemical studies and for switching experiments, a potential of -0.5 V was applied. Radiation from solar simulator (light flux = 100 mW/cm²) was used for these studies.

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