Photocatalytic Hydrogen Production from H$_2$S using Nanostructured CNT blended CdZnS/Fe$_2$O$_3$ Thin Film on Glass Substrate

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Abstract. A co-precipitation method was employed to prepare the CNT blended CdZnS/Fe$_2$O$_3$ photocatalyst. Using the powder photocatalyst, the thin film of CNT blended CdZnS/Fe$_2$O$_3$ photocatalyst over a glass substrate was prepared using the drop-casting method. The obtained thin film was characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), energy-dispersive X-ray analysis (EDAX), photoluminescence (PL), and hydrogen production activity studies in order to obtain information on their structural, morphology, chemical composition, optical and hydrogen production efficiency. The hydrogen production activity of catalyst or effective conversion of H$_2$S into hydrogen (H$_2$) and sulfur (S) using thin-film photocatalyst was evaluated using a simulated sulfide solution. The results showed that 1 mg of CNT blended CdZnS/Fe$_2$O$_3$ catalyst coated as thin film over glass substrate (4.69 cm$^2$) showed the highest hydrogen production value of 3180 µmol h$^{-1}$g$^{-1}$; compared to that of 1 mg CNT blended CdZnS/Fe$_2$O$_3$ powder of 2510 µmol h$^{-1}$g$^{-1}$. From the above results, it is concluded that the thin film form of photocatalyst produced more hydrogen than the powder form. This is attributed to the effective charge separation and increased specific surface area in thin film photocatalyst.

1. Introduction

Hydrogen sulfide (H$_2$S) is a toxic substance produced by natural and industrial sources in large quantities [1-4]. Most of the new industrial technology for the extraction of H$_2$S is an absorption/stripping method using aqueous ethanolamine solutions, followed by Claus process for the decomposition of H$_2$S into water and sulfur [5]. But because of the high cost, this is not an economically viable operation and the process actually results further environmental problems [6]. Different strategies have been suggested transforming H$_2$S into hydrogen and sulfur to address environmental issues and hydrogen production. The most promising beneficial method to address the environmental problems and production of clean energy (H$_2$) is a direct splitting of H$_2$S to generate H$_2$ and S using visible light-responsive photocatalyst. Here we found that CNT blended CdZnS/Fe$_2$O$_3$ thin film photocatalyst can effectively convert H$_2$S into H$_2$ and S.
2. Experimental

2.1. Synthesis of CNT and (CdZnS)/Fe₂O₃ nanoparticles

CNT has been synthesized by the co-precipitation method using H₂ and acetylene gas as the precursor materials and Fe+Mo/MgO as the catalyst. Similarly, CdZnS coated Fe₂O₃ was prepared by the co-precipitation method [7].

2.2. Synthesis of CNT blended (CdZnS/Fe₂O₃)

CNT (4%) blended (CdZnS)/Fe₂O₃ was prepared by mixing CdZnS/Fe₂O₃ (0.96 g) and CNT (0.04 g) followed by calcination at 400 ºC.

2.3. Preparation of thin film photocatalyst over glass plate

The hydrogen production activity studies was performed with 1.25 x 3.75 cm² size thin film. The drop-casting method was used to make the thin film of CNT/(CdZnS/Fe₂O₃) photocatalyst over the glass plates without the addition of any binders. The photocatalyst and ethanol in 1:1 ratio (1 mg of photocatalyst +1 mL of ethanol) have been taken and sonicated for 10 minutes to get uniform dispersion of the catalyst. Then the dispersion was drop-casted continually on the glass plate using 100 mL micropipette and dried under room temperature for 12 h.

2.4. Characterization of CNT/(CdZnS/Fe₂O₃)

The structural properties of the prepared photocatalyst were characterized by X-ray Diffractions–Panalytical model using Radiation Cu-Kα, Goniometer Type: Vertical, Range of 2θ. The surface morphology, Chemical composition and weight percentage of the photocatalyst were analyzed using Scanning electron microscope with EDAX (CoXem). Photoluminescence (PL) performance was analyzed using UV-VIS-NIR Spectrofluorometer (JASCO FP 8600). Agilent 7890A gas chromatograph (GC) equipped with a thermal conductivity detector at 200ºC was used to study the hydrogen production activity.

3. Results and Discussion

3.1. Structural Study

X-ray diffraction (XRD) analysis was conducted to assess the structure of the thin film containing CNT blended CdZnS/Fe₂O₃. As observed in Figure 1, 11 reflection peaks appeared. The pattern shows peaks with 20 values of 26.5° and 43.6° corresponding to (002) and (100) reflection which is confirmed the presence of CNT (JCPDS card No.75-1621) [8]. The peaks at 24.3°, 29.0°, 52.2°, 57.7° can be well indexed to the lattice planes (012), (101), (200), (040) respectively, which were attributed to CdS+ZnS (JCPDS no.49-1302) [9]. Similarly the characteristic peaks at 33.3°, 35.8°, 46.6°, 62.5° and 64.1° corresponding to the lattice planes (104), (110), (113), (214) and (300) respectively, which attributed to Fe₂O₃ (JCPDS no. 89-2810) [10]. The crystallite size of the photocatalyst was determined by Scherer’s formula and it is found to be 4.23 nm.
3.2. Chemical Analysis

A scanning electron microscope (SEM) was used to study the surface morphology and microstructural characteristics of the CNT/(CdZnS/Fe$_2$O$_3$) thin film deposited on glass substrate (Figure 2). The CNT/(CdZnS/Fe$_2$O$_3$) thin film micrograph shows a compact structure consisting of a single type of small, densely packed microcrystals. It can be observed that the grains are spherical, well defined, and consist almost similar size.

Figure 3 depicts the typical energy dispersive X-ray analysis (EDAX) spectra of CNT blended CdZnS/Fe$_2$O$_3$. EDAX result shows the presence of cadmium (Cd), zinc (Zn), sulphur (S), iron (Fe), oxygen (O) and carbon (C) [11-13]. The weight percentage of Cd, Zn, S, Fe, C and O are 47.92, 11.77, 11.40, 1.50, 25.84 and 1.57, respectively. The weight percentage of Fe is relatively less and it is more difficult to see due to the core-shell formation.

![XRD pattern of the CNT blended CdZnS/Fe$_2$O$_3$ thin film.](image1.png)

**Figure 1.** XRD pattern of the CNT blended CdZnS/Fe$_2$O$_3$ thin film.

![SEM image of CNT blended CdZnS/Fe$_2$O$_3$ thin film](image2.png)

**Figure 2.** SEM image of CNT blended CdZnS/Fe$_2$O$_3$ thin film.
3.3. **Photoluminescence studies**

Figure 4 shows the room temperature PL spectra of both powder and thin CNT blended CdZnS/Fe$_2$O$_3$ noted with an excitation wavelength of 200 nm. It is found out that there was a decrease in the PL signals of thin-film photocatalyst compared to powder catalyst. In general, the lower the PL intensity, the lower the recombination rate of charge carriers (electron-hole pairs), and the higher the photocatalytic activity [14, 15].

3.4. **Solar hydrogen production activity**

The hydrogen production activity of the thin-film catalyst CNT blended CdZnS/Fe$_2$O$_3$ was evaluated under solar simulator for 2 hours using a simulated sulfide solution (0.2M of sulphide + 0.2M of sulfite solution), the produced gas was analysed using gas chromatography. The results obtained and area report are shown in Figure 5 and Table 1.
Figure 5. Hydrogen production activity using gas chromatography

Table 1. Area report obtained from the gas chromatogram.

| Retention Time | Area   | Area % | Height | Height % |
|----------------|--------|--------|--------|----------|
| 0.891          | 2326482| 100.00 | 691795 | 100.00   |

\[
\frac{\text{Area}}{\text{Slope}} = x \\
\text{x} \times \text{dead space} \times 2 = y \\
\frac{y}{\text{hr}} = z \ \mu\text{mol/hr} \\
\frac{z}{\text{mg}} = \ldots \mu\text{mol/hr/mg}
\]

Where, Slope = 21866068 and dead space = 30

The 1 mg of powder form of CNT blended CdZnS/Fe₂O₃ catalyst coated over 4.69 cm² (thin film) showed the highest hydrogen production value of 3180 µmol h⁻¹ g⁻¹.

4. Conclusion
In this study, we found that the thin film photocatalyst was effectively converting H₂S into hydrogen (H₂) and sulfur (S). The thin film CNT blended CdZnS/Fe₂O₃ photocatalyst has been synthesized using a simple drop-casting method. Hydrogen production activity study was carried out using simulated sulfide solution. The 1 mg of powder form catalyst showed hydrogen production of about 2510 µmol h⁻¹ g⁻¹ whereas the same amount of photocatalyst in thin-film outperformed (3180 µmol h⁻¹ g⁻¹). This study will be helpful in implementing the photocatalytic hydrogen production on a large scale using thin-film under direct sunlight.

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