

Photocatalytic hydrogen evolution from ZnO-loaded carbon nanotube

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Abstract: Graphene-based materials attract important interest due to their enhanced electron transfer efficiency in photocatalytic hydrogen evolution reactions. In this study, 1D graphene-based nanomaterial combined with ZnO and produced heterostructured CNT/ZnO nanocomposite catalyst enhance the hydrogen evolution. Herein, co-catalysts (MoS_x and Pt) were photodeposited onto CNT/ZnO nanocomposite catalyst in water, resulting in the formation of CNT/ZnO/MoS_x and CNT/ZnO/Pt through the reduction of (NH₄)₂MoS₄ and H₂PtCl₆.6H₂O, respectively. The photodeposition of co-catalysts on the CNT/ZnO nanocomposite provided enhanced catalytic efficiency and stability due to increased active surface area and enhanced electron transfer capabilities. CNT/ZnO/MoS_x photocatalysts are one of the most promising, clean and sustainable energy carrier for photocatalytic hydrogen production.

Keywords: photodeposition, photocatalytic activity, hydrogen, graphene-based nanomaterials

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1. Introduction

The importance of renewable energy sources has become increasingly important due to the growing global energy demand. Photocatalytic hydrogen evolution reactions (HERs) have emerged as a significant solution in this context (Teets and Nocera 2011; Preethi and Kanmani 2013). Among the semiconductor catalysts investigated to enhance photocatalytic hydrogen production, ZnO stands out as an effective photocatalyst for hydrogen production due to its stability in the chemical reactions, abundance, improved charge mobility and safety in the reactions. But, ZnO has limited hydrogen production efficiency due to high exciton formation rate, limited surface area for mass transfer, hydrogen evolution under UV light irradiation, and wide band gap (3.19 eV) (Yuan et al. 2015). In order to overcome these challenges, heterostructured photocatalysts have been proposed to improve the photocatalytic activity of ZnO catalyst. Graphene-based materials are considered as promising candidates for these heterostructures due to their superb specifications. The incorporation of ZnO with graphene-based materials has been extensively investigated to enhance the photocatalytic activity. Among these affordable graphene-based materials, carbon nanotubes (CNTs) have been used in photocatalytic studies, can

effectively act as electron donors/acceptors by extending the lifetime of electron-hole pairs in HERs. Graphene-derived materials have been used in catalytic studies such as degradation, hydrogen production and decontamination due to their properties such as large surface area, strong adsorption capacity and charge density. In various studies, graphene derivatives have been combined with ZnO to improve the hydrogen production activity (Dhiman et al. 2022). There are some works in the literature on the effect of the combination of ZnO and CNTs in photocatalytic HERs. According to the literature, the combination of ZnO with CNTs effectively improves hydrogen evolution, but there are some shortcomings such as low visible light absorption, high photocorrosion, low stability and incomplete photocatalytic mechanism. In the study, the hydrogen evolution efficiency of ZnO/CNTs was improved by forming a heterostructure with Sr doping. Heterojunction provides increased light absorption, improved charge separation, and optimizes optical band gap for enhanced hydrogen production (Ahmad et al. 2021). In another study, hydrothermally synthesized CNT/ZnO/TiO₂ catalyst was used the degradation of asid orange (Bai et al. 2015). Bakos and coworkers deposited the TiO₂ and ZnO on CNT with the help of atomic layer deposition method. CNT/TiO₂/ZnO

were used in the methyl orange degradation (Bakos et al. 2020). Hydrothermally synthesized yttrium doped CNT/ZnO catalyst improve the degradation efficiency of methylene blue dye (Sharma et al. 2021). Another study, ZnO/CNT nanocatalyst used on the glass photoelectrodes result in the improved chemical stability, lowered corrosion and enhanced electrochemical productivity (Alenad et al. 2023). In the another study, the synthesized CNT/ZnO core-shell nanostructures were used in the electrochemical photocatalytic HERs and prevent the photocorrosion and improve catalyst stability (Prasadam et al. 2022). In photocatalytic studies, photodeposition of cocatalyst has been intensively investigated as it increases catalytic efficiency by both enhancing electron transfer activity and expanding surface area. Platinum (Pt) is among the cocatalysts used to enhance hydrogen production due to its large surface area and efficient electron transfer activity. For example, deposition of Pt nanoparticles onto CNTs via chemical photodeposition has shown improved hydrogen production rates by inhibiting electron-hole recombination. However, the high cost of Pt, being a noble metal, limits its use in large-scale studies. Recently, molybdenum sulfides (MoS_x) have been offered as a cost-effective alternative cocatalyst to Pt with similar catalytic activity. MoS_x contains sulfur atoms that provide abundant electron transport channels and active surface area, leading to enhanced photocatalytic HER activity. In one study, CNTs/ZnO/ MoS_2 ternary nanocomposite was used for the degradation of aniline (Ghasemipour et al. 2020). To our knowledge, there are no photocatalytic hydrogen evolution studies in the literature regarding MoS_x and Pt photodeposition on CNT/ZnO catalysts. In this study, synthesized CNT/ZnO nanocomposite was used as a photocatalyst in the HERs to enhance the hydrogen evolution reaction. MoS_x and Pt were photodeposited onto CNT/ZnO nanocomposite catalyst in water, resulting in the formation of CNT/ZnO/ MoS_x and CNT/ZnO/Pt through the reduction of $(\text{NH}_4)_2\text{MoS}_4$ and $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, respectively. The photodeposition of MoS_x and Pt on the CNT/ZnO composite provided improved photocatalytic activity and stability because of enlarged surface area and improved electron transfer ability.

2. Materials and Method

2.1. Materials

Zinc acetate (99.99%, $\text{Zn}(\text{CH}_3\text{CO}_2)_2$), oleylamine ($\geq 98\%$, OLA) and Ethanol [absolute, $\geq 99.8\%$] were supplied from Sigma-Aldrich. Multi-walled carbon nanotube (99.99%; (MWCNT) was provided from Nanografi. Triethanolamine (TEOA, $> 98\%$), hydrochloric acid (HCl), chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$), ammonium tetrathiomolybdate ($(\text{NH}_4)_2\text{MoS}_4$), eosin-Y (EY $> 95\%$) were purchased by Sigma-Aldrich.

2.2. Methods

2.2.1. Synthesis of ZnO and CNT/ZnO Catalysts

0.5 mmol $\text{Zn}(\text{CH}_3\text{CO}_2)_2$ and 15 mL OLA were mixed in a 50 mL beaker until the temperature reached 280°C . After the cooling of mixture, ethanol/toluene mixture (5/15 mL)

was added to the synthesis medium and precipitated by centrifugation at 3000 rpm for 1 minute. In the last step, the precipitate formed was washed with ethanol and left to dry. In the synthesis of ZnO/CNT composites, 1 mg carbon source was put to the beaker in the first stage of the synthesis (Genç et al. 2023b).

2.2.2. Photocatalytic Hydrogen Evolution Reactions

The study focuses on generating hydrogen through a photocatalytic water-splitting reaction by depositing cocatalysts (MoS_x and Pt) onto CNT/ZnO composite. This is achieved by reducing precursors, $(\text{NH}_4)_2\text{MoS}_4$ and $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$. To enhance the efficiency of hydrogen production and prevent the formation of oxygen, TEOA in aqueous solutions was used as an electron donor. The objective is to create composites like CNT/ZnO/Pt and CNT/ZnO/ MoS_x the photodeposition method, improving the efficiency of the reaction and utilizing CNT/ZnO composite catalyst. Furthermore, after analyzing the optical and electrochemical properties of the ZnO structure, visible light sensitization was performed using EY, a well-known dye, to resolve issues with light absorption and electron transfer, or to increase light absorption. The reaction cell containing the CNT/ZnO composite and salts was placed inside an anaerobic glovebox, combined with an electron donor solution under an inert nitrogen atmosphere and sealed with a rubber septum to isolate it from the external environment. Sonication in a water bath was conducted to ensure the catalysts were well dispersed in the electron donor solution. After, the reaction cell was positioned under a visible light source and continuously stirred with a magnetic stirrer to ensure uniform reaction progress. Periodically, gas samples were taken from the top of the reaction cell using a syringe and analyzed with gas chromatography to determine the amount of hydrogen produced, which was then calculated using a calibration curve. By optimizing conditions such as pH, electron donor concentrations and dye concentrations, the catalytic parameters were determined under optimal conditions. The photocatalytic hydrogen production was also tested without the use of dye or electron donors for comparison. The solar-to-hydrogen conversion efficiency (STH) was evaluated using the specified equation (Eq.1) (Genç et al. 2023b; Genc et al. 2024).

$$\text{STH \%} = \frac{\Delta G^\circ \times R_{\text{H}_2}}{P \times A} \times 100 \quad \text{Eq.1}$$

In this equation, P and A refers to the irradiation power density of incident light and the irradiated area (cm^2) by incident light, respectively. Moreover, R_{H_2} and ΔG° indicates the hydrogen production rate (mmol s^{-1}) and the Gibbs free energy standard (237 kJ mol^{-1}) for water splitting reactions, respectively.

3. Results

The X-ray diffraction (XRD) analysis was conducted to examine the structures and crystallinity of the photocatalysts. The XRD analysis results of bare ZnO and CNT/ZnO composites are shown in Fig 1. Clearly

understand that all diffraction peaks of CNT/ZnO and ZnO catalysts are comprehend with reference values (089-1397).

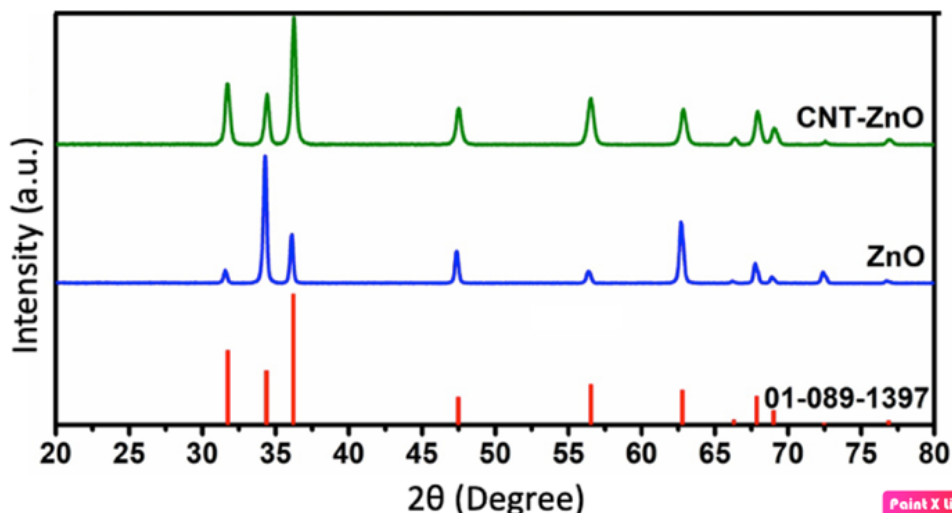


Fig 1. XRD results of ZnO ve CNT/ZnO photocatalysts

It is understood that carbon sources acted as catalysts during the reaction and enhanced crystallinity, resulting in patterns that are more consistent with reference diffraction peak values checked against to pure ZnO. In addition, since the amount of CNT was considerably lower than that of ZnO, diffraction peaks belonging to the CNT phase could not be detected in the XRD graph. The diffraction peaks at 31.6, 34.5, 36.2, 47.5, 56.5, 62.8, 66.2, 67.9, 69.1, 72.5, and 76.9 degrees were matched with the (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), and (202) planes of hexagonal crystal system. Additionally, the absence of peaks from other phases indicates that the syntheses were successfully carried out.

The optical properties of the CNT/ZnO catalyst were analyzed using diffuse reflectance spectroscopy. Firstly, diffuse reflectance measurements were taken and the obtained data were converted into absorption spectra using the Kubelka-Munk equation (Fig 2). According to the results, CNT/ZnO and ZnO catalysts exhibit similar reflection and absorption properties. To determine the band

gap values of the catalysts, $(F(R_{\infty})/h\nu)^2$ vs. $h\nu$ plots were constructed. The band gap of the ZnO (Fig 2(a)) and CNT/ZnO (Fig 2(b)) was calculated to be 3.24 and 3.21 eV, respectively.

The morphological properties of the CNT/ZnO catalyst were analyzed using scanning electron microscopy (SEM) and energy dispersive spectrophotometry (EDX), and the results are shown in Fig 3. According to these results, pure ZnO particles, which are hexagonal shape, were found to form triangular and spherical ZnO particles during the composite form (Fig 3(a)). This variation in shapes was influenced by the type of carbon source and led to the particles growing in different directions. Moreover, EDX result confirm the synthesized ZnO particle composition is very close the ideal value (Fig 3(b), (c)). These results indicate that ZnO particles with shape control can be achieved depending on the type of carbon source. The EDX results shown in Fig 3(d) also demonstrate that the ingredient of the composites is so similar to ideal EDX values.

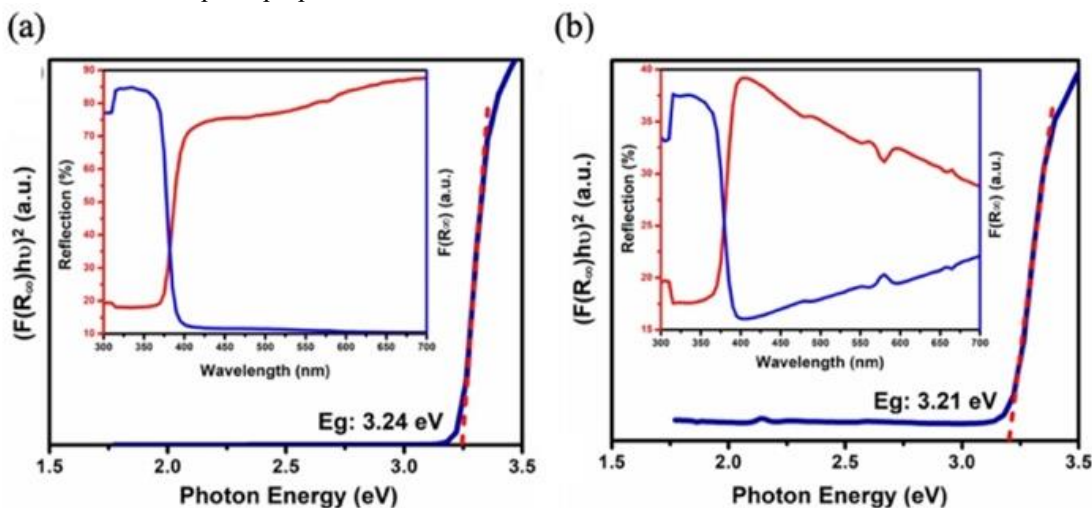
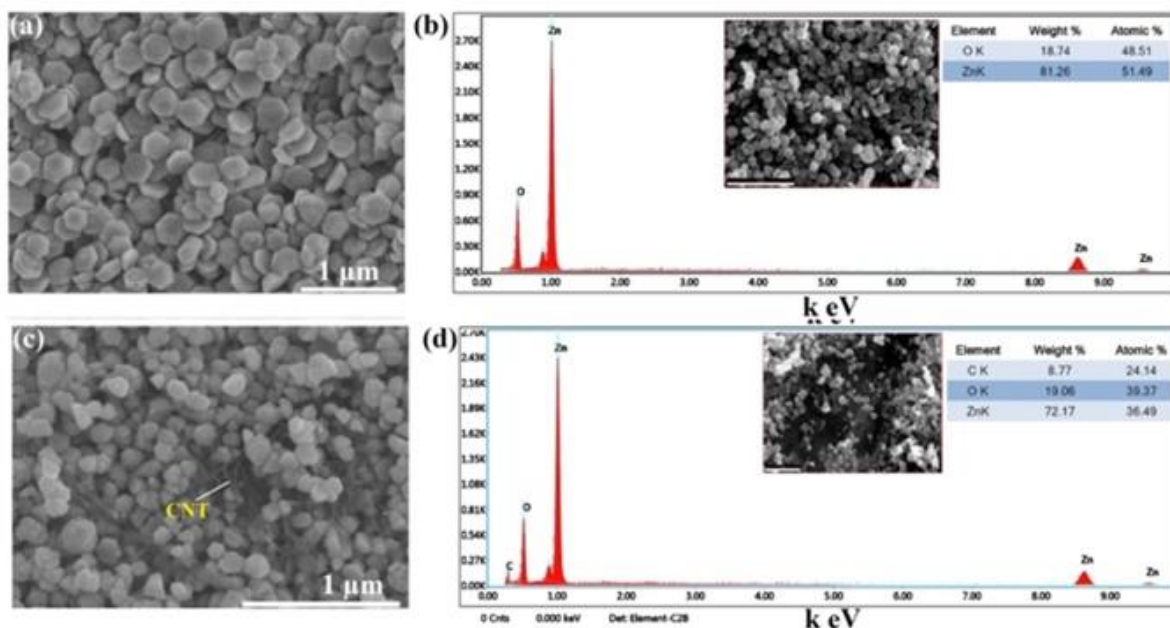


Fig 2. The diffuse reflection and Kubelka-Munk function graph of ZnO (a), and CNT/ZnO (b)**Fig 3.** SEM (a), (c) ve EDX (b), (d) results of bare ZnO and CNT/ZnO catalysts

Photocatalytic hydrogen production studies for CNT/ZnO, CNT/ZnO/Pt and CNT/ZnO/MoS_x photocatalysts were conducted in an aqueous solution using EY (photosensitizer) and TEOA (electron donor). The hydrogen production tests for the photocatalysts were performed over periods ranging from 1 hour to 8 hours (Fig 4(a)). Photocatalysts are unable to produce hydrogen in the dark condition because they cannot supply the energy required for photocatalytic reactions to take place. The hydrogen production from pure CNT and pure ZnO was below the calibration curve, so they could not be calculated, and the trace amounts of hydrogen produced were disregarded. It is clear that CNT/ZnO, as a carbon source-loaded composite material, improves hydrogen production compared to pure ZnO. After 1 hour of irradiation, the photocatalytic hydrogen production rate of the CNT/ZnO composite catalyst was measured as 654 $\mu\text{mol h}^{-1}\text{g}^{-1}$. After 8 hours of reaction, the photocatalytic hydrogen production from the CNT/ZnO catalyst increased to 5119 $\mu\text{mol g}^{-1}$. The hydrogen production of CNT/ZnO/Pt catalyst was reached from 1432 $\mu\text{mol h}^{-1}\text{g}^{-1}$ to 3692 $\mu\text{mol g}^{-1}$ after 8 hours light irradiation. Moreover, the hydrogen production rate of CNT/ZnO/MoS_x catalyst was reached from 4121 $\mu\text{mol h}^{-1}\text{g}^{-1}$ to 46696 $\mu\text{mol g}^{-1}$ after 8 hour illumination. The *in situ* photodeposition was performed the reduction of (NH₄)₂MoS₄ and H₂PtCl₆·6H₂O precursors onto CNT/ZnO catalyst result in improved hydrogen production activity and stability. CNT/ZnO/Pt and CNT/ZnO catalysts were found to produce similar amount of hydrogen. However, CNT/ZnO/MoS_x photocatalyst produce hydrogen approximately 9 times higher than CNT/ZnO catalyst. The 1D nanocomposite catalyst, CNT/ZnO, provides higher conductivity and enhances charge transfer. Additionally, the photocatalysts UV-Vis absorption spectroscopy results are shown in Fig 4(b). The different hydrogen production

amount the used composite catalysts are understood by the degradation of EY, as indicated by the UV-Vis spectra measured before and after the photocatalytic reaction. It was observed that the characteristic absorption peak of the EY dye solution at 520 nm shifted to 490 nm after 8 hours of irradiation. In other words, compared to pure ZnO, carbon-loaded nanocomposites showed a red-to-blue shift after 8 hours of irradiation. The UV-Vis spectrum analysis results are consistent with the hydrogen production reaction results, and it is shown that the CNT/ZnO/MoS_x catalyst has a higher absorption peak than the CNT/ZnO and CNT/ZnO/Pt composite catalysts. According to the STH efficiency results, the STH values for the CNT/ZnO, CNT/ZnO/Pt and CNT/ZnO/MoS_x composite catalysts were calculated to be 1.68%, 1.19%, and 15.05%, respectively.

The suggested photocatalytic hydrogen evolution mechanisms of CNT/ZnO/(MoS_x or Pt) catalyst were shown in the **Figure 5**. Under visible light, photons were absorbed by EY and photogenerated electrons were transferred from HOMO level to LUMO level of EY dye (-1.1 V). Since generated electrons cannot be excited in the dark condition, hydrogen production does not take place. The excited electrons then transferred from sensitizers' LUMO to CNT catalyst. These excited electrons can be employed in two distinct reactions: the photodeposition of MoS_x and the reduction of water through transfer from CNT to ZnO. When the absence of co-catalyst, electron-hole pairs have a tendency to create exciton formation, which lowers photocatalytic hydrogen evolution activity. CNT/ZnO nanocomposite by employing MoS_x and Pt co-catalysts precursors utilizing (NH₄)₂MoS₄ and H₂PtCl₆·6H₂O, respectively. At the same time, TEOA can replenish the excited form of EY by providing electrons. The enhanced hydrogen evolution rate of the CNT/ZnO/MoS_x

nanocomposite is almost 9 times, higher than that of the pure CNT/ZnO nanocomposite. Photo-excited electrons can be transferred to the co-catalyst across the CNT/ZnO catalyst when there is a MoS_x co-catalyst present in the media. This reduces the protons that are absorbed by

unsaturated S atoms to H₂ (Genç et al. 2023a). Because of the abundance of unsaturated S²⁻, terminal S₂²⁻, bridging S²⁻/S₂²⁻ and apical S₂²⁻ of amorphous MoS_x, the proton can be readily trapped by MoS_x, leading to increased photocatalytic evolution activity (Sekar 2023).

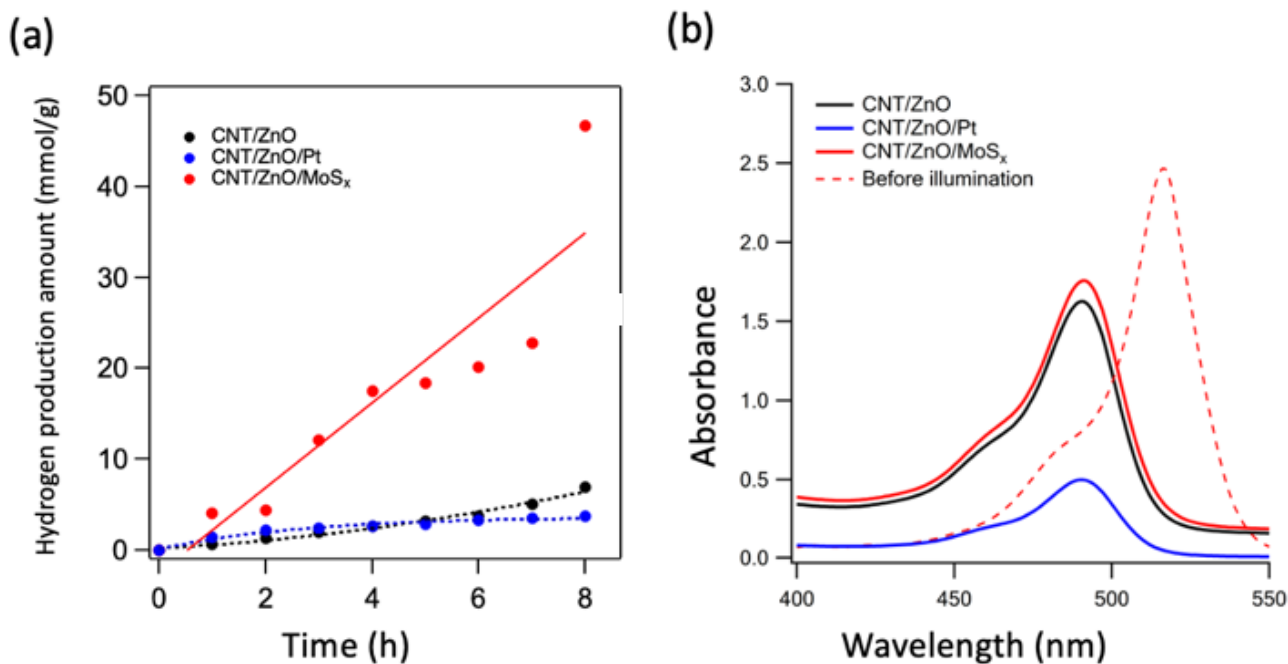


Fig 4. Photocatalytic study results of CNT/ZnO, CNT/ZnO/Pt, and CNT/ZnO/MoS_x (a), UV-Vis absorption spectra of the reaction solution before and after illumination (absence/presence of CNT/ZnO, CNT/ZnO/Pt, and CNT/ZnO/MoS_x composite catalysts) (b)

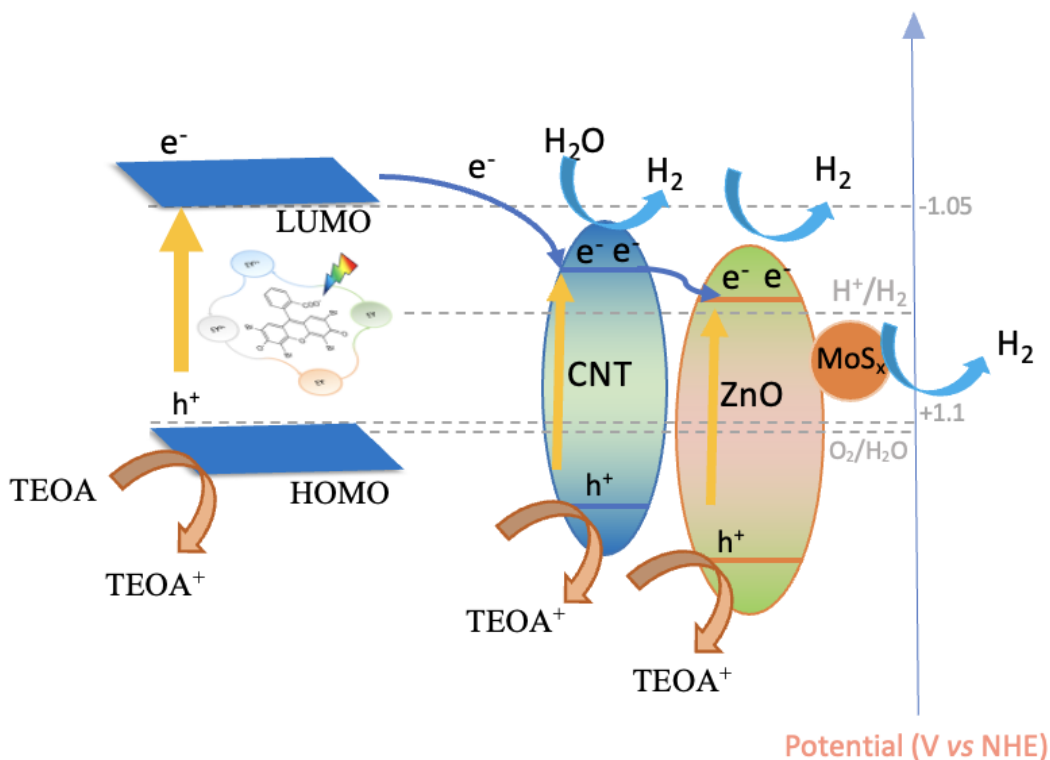


Figure 5. Suggested photocatalytic hydrogen evolution mechanism of CNT/ZnO/MoS_x catalyst

4. Discussion

In this study, hydrogen production was increased by facilitating electron transfer activity and increasing electron-hole separation efficiency by photodeposition of MoS_x and Pt co-catalysts on CNT/ZnO nanocomposite catalyst. The boosted production activity of the light-deposited catalysts could be associated with an enlarged surface, eased charge separation efficiency, formation of unsaturated S atoms, and a low exciton formation rate (Genç et al. 2023a). According to literature, CNTs were used in many photocatalytic studies to enhance the efficiency of the hydrogen production (Ahmad et al. 2021; Wang, Li, et al. 2020; Wang, Wang, et al. 2020; Haldorai and Shim 2014). Carbon based materials prevent exciton formation, enlarge active surface area result in improved hydrogen evolution reaction in the hydrogen evolution reaction (Ahmad et al. 2021). Furthermore, Pt photodeposition on the CNT/TiO₂ catalyst improves the hydrogen evolution efficiency by providing eased charge separation, enlarged active surface area, lowered recombination rate in the photocatalytic HERs (Chen et al. 2015). Compared with these studies, the significant efficiency of the CNT/ZnO/MoS_x composite (15.05%) underscores the effective role of the co-catalysts in enhancing photocatalytic performance, while the lower efficiencies of the CNT/ZnO and CNT/ZnO/Pt composites indicate areas for further optimization. Significant hydrogen production efficiency increases the importance of CNT/ZnO/MoS_x composite catalyst for catalytic studies. In this study, photodeposited catalyst activity highlighted its potential to be considered as an alternative material for future studies.

5. Conclusion

In conclusion, the photodeposition of MoS_x and Pt co-catalyst onto the CNT/ZnO catalyst was carried out successfully. These results show that, photodeposition of co-catalyst can improve electron transfer, electron-hole separation ability and lead to increased hydrogen production. The boosted production activity of the light-deposited catalysts could be associated with a enlarged surface, eased charge separation efficiency, formation of unsaturated S atoms, and a low exciton formation rate. In particular, the STH value of the CNT/ZnO/MoS_x composite catalyst clearly demonstrates the catalytic activity of this material and its importance for catalytic studies. Additionally, this work opens the door for exploring alternatives to widely known carbon-based nanomaterials, carbon nanotubes, in nanocomposite formation. Eventually, this study will also enable the design and production of nanocomposites for different applications using various organic and inorganic substrates that do not contain carbon.

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Authors' contributions: MTG; designed research, performed hydrogen evolution experiments, write the paper and edit the final version of paper, IHP; designed research, edit the final version of paper, AS; synthesized and characterized nanocomposites and edit the final version of paper, FO; synthesized and characterized nanocomposites, edit the final version of paper, EA; edit the final version of paper. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Conflict of interest disclosure:

There is no conflict of interest.

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