

Article

One-Pot Facile Synthesis of $\text{ZrO}_2\text{-CdWO}_4$: A Novel Nanocomposite for Hydrogen Production via Photocatalytic Water Splitting

Ahmed Hussain Jawhari 

Department of Chemistry, College of Science, Jazan University, P.O. Box 114, Jazan 45142, Saudi Arabia; ahjawhari@jazanu.edu.sa

Abstract: ZrO_2 -based nanocomposites are highly versatile materials with huge potential for photocatalysis. In this study, $\text{ZrO}_2\text{-CdWO}_4$ nanocomposites (NC) were prepared via the green route using aqueous *Brassica rapa* leaf extract, and its photocatalytic water-splitting application was evaluated. *Brassica rapa* leaf extract acts as a reducing agent and abundant phytochemicals are adsorbed onto the nanoparticle surfaces, improving the properties of $\text{ZrO}_2\text{-CdWO}_4$ nanocomposites. As-prepared samples were characterized by using various spectroscopic and microscopic techniques. The energy of the direct band gap (E_g) of $\text{ZrO}_2\text{-CdWO}_4$ was determined as 2.66 eV. FTIR analysis revealed the various functional groups present in the prepared material. XRD analysis showed that the average crystallite size of ZrO_2 and CdWO_4 in $\text{ZrO}_2\text{-CdWO}_4$ was approximately 8 nm and 26 nm, respectively. SEM and TEM images suggested ZrO_2 deposition over CdWO_4 nanorods, which increases the roughness of the surface. The prepared sample was also suggested to be porous. BET surface area, pore volume, and half pore width of $\text{ZrO}_2\text{-CdWO}_4$ were estimated to be $19.6 \text{ m}^2/\text{g}$, 0.0254 cc/g , and $9.457 \text{ \AA}$, respectively. PL analysis suggested the conjugation between the ZrO_2 and CdWO_4 by lowering the PL graph on ZrO_2 deposition over CdWO_4 . The valence and conduction band edge positions were also determined for $\text{ZrO}_2\text{-CdWO}_4$. These band positions suggested the formation of a type I heterojunction between ZrO_2 and CdWO_4 . $\text{ZrO}_2\text{-CdWO}_4$ was used as a photocatalyst for hydrogen production via water splitting. Water-splitting results confirmed the ability of the $\text{ZrO}_2\text{-CdWO}_4$ system for enhanced hydrogen production. The effect of various parameters such as photocatalyst amount, reaction time, temperature, water pH, and concentration of sacrificial agent was also optimized. The results suggested that 250 mg of $\text{ZrO}_2\text{-CdWO}_4$ could produce $1574 \text{ }\mu\text{mol/g}$ after 5 h at 27°C , pH 7, using 30 vol. % of methanol. $\text{ZrO}_2\text{-CdWO}_4$ was reused for up to seven cycles with a high hydrogen production efficiency. This may prove to be useful research on the use of heterojunction materials for photocatalytic hydrogen production.

Keywords: nanocomposite; heterojunction photocatalyst; $\text{ZrO}_2\text{-CdWO}_4$; water splitting; H_2 production



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1. Introduction

Increasing populations and modernization, human dependence on energy is increasing continuously, and this is becoming a burden on the global environmental system, as most of the energy is generated from fossil fuels [1]. Various nations have been raising issues of pollution and energy crisis, which is why alternative means of developing renewable and clean energy systems are constantly being explored [1,2].

Hydrogen (H_2) gas, which acts as a secondary energy source, holds a significant position in this aspect [3]. H_2 has advantages over other energy resources, because of its lightweight, high calorific value, and pollution-free clean combustion [4]. Since hydrogen gas can be a green source of energy, new and easier methods of production are constantly being discovered; however, currently with the existing technologies, the H_2 production method is quite expensive [5].

Various methods have been adopted for H_2 production such as petroleum-based petrochemical processes [6], steam reforming of methane or propane [7], thermal decomposition

of water by nuclear energy [8], solid electrolysis [9], biomass gasification [10] and splitting of water [11].

H₂ production via water electrolysis or water splitting holds a clear edge over other contemporary methods since it does not emit secondary pollution [9,11,12]. Production of H₂ by the water-splitting process on the surface of the photocatalyst in the presence of light is being recognized as the most advanced and resourceful technology [12]. The most commonly used materials to streamline this process are nanosized semiconductors that act as photocatalysts and prove to be promising candidates due to their unique physical and optical properties [13]. Despite having many properties, the drawback of these nanomaterials is their inability to work better in the presence of visible or natural solar light [14,15].

Generally, a photocatalyst directly absorbs a major portion of sunlight for efficient H₂ production. This requires a suitable band gap. A larger-band-gap photocatalyst absorbs sunlight mainly in the UV region. For example, TiO₂ was determined to be a stable and efficient photocatalyst for producing H₂ but its larger band gap (>3 eV) limits light absorption [14,15]. It is known that photocatalysts produce electrons and holes in the presence of light, which are responsible for the photolysis process; however, due to the large band gap in the photocatalyst or due to reduced charge separation or high electron-hole recombination, their efficiency is nullified [15]. These shortcomings ultimately reduce the yield potential and photocatalytic properties of such materials under natural solar light. This may not prove useful considering H₂ production requirements [15].

In view of the above deficiency, many upgradations have been made, the most useful is the development of heterojunction composite materials [16–18]. Heterojunction composites have better optical properties due to new crystallographic phases than the original oxides, the creation of defect energy levels in the band gap region, and changes in the surface characteristics of the individual oxides due to the formation of new sites at the interface of the components, increasing the stability of the photoactive crystalline phase [16–18].

From a photocatalytic point of view, coupling two materials leads to the formation of a heterojunction with different positions of energy bands. Previous studies have suggested that there can be three types of heterojunctions depending on the position of the band edge such as straddling gap (type I), staggered gap (type II) or broken gap (type III) [19]. Currently, a type I heterojunction is considered attractive and advanced, responsible for many benefits such as a narrow energy band gap, prevention of recombination of photo-generated electron holes, and charge separation [19]. This further allows them to capture solar/visible light efficiently and smooth and long-term circulation of photogenerated electrons and holes over the surface, and ultimately increases the photocatalytic efficiency of materials [16–18].

To practically verify this subject and to increase the importance of the H₂ production method, this study was conducted, in which two bare semiconductors (CdWO₄ and ZrO₂) with a large energy band gap were coupled to the developed heterojunction.

Notably, monoclinic wolframite CdWO₄ is known for good photocatalytic performance due to its layered structure, self-trapped excitons, optical, chemical, and structural properties, and thermal stability. But modified (doped or coupled) CdWO₄ may have better photocatalytic performance than bare CdWO₄ due to a wider band gap in bare CdWO₄ (~3.5–4.0 eV) [16–18]. For instance, Yogesh and others reported nanostructured CdS-sensitized CdWO₄ nanorods that exhibited highly efficient H₂ generation than bare CdWO₄ [20].

In addition to CdWO₄, ZrO₂, a n-type semiconductor, received much attention due to its substantial amount of oxygen vacancies, strong ion exchangeability, and physico-chemical stability. However, it is a broad-band-gap semiconductor (5.5 eV) that requires UV-C light (<280 nm) for electron-hole generation [21]. One method to overcome this problem is by doping ZrO₂ with different transition metal ions or coupling with other metal oxides, creating composites, bringing about heterojunction formation, and incorporating co-catalysts. For instance, a binder-free WS₂/ZrO₂ hybrid nanocomposite (NC)

was reported as a photocatalyst for H_2 production via water splitting [22]. The coupling of ZrO_2 with other semiconductors like SiO_2 , TiO_2 , ZnO , WO_3 , and NiO have also been reported [23,24].

Considering the advantages of both these materials as bare photocatalysts, along with their composites, this study assessed the photocatalytic activity of the heterojunction material developed by coupling ZrO_2 and $CdWO_4$.

Many methods like coprecipitation [25], hydrothermal [26], sol–gel [27], microwave [28], and bioprecipitation [16] have been used to develop heterojunction material. However, among all these methods, bioprecipitation is the cheapest, easiest, sustainable, and green [17,21], hence the bioprecipitation method has been chosen as the synthesis method in the present study.

In the bioprecipitation method, plant extracts were used, which act as reducing, capping, and stabilizing agents [16–18,29–31]. The plant extracts are usually a rich source of phytochemicals that adsorb onto the material surface during preparation and enhance the properties of materials such as a stabilized particle, reduced particle size, enhanced surface functional sites, and large surface area [16–18,21,32]. The presence of functional groups on the surface of the material also enhances the photocatalytic activity of the material by easily absorbing sunlight [16–18].

Keeping all these features in mind, the green method was adopted for the present (ZrO_2 - $CdWO_4$) preparation for which leaf extracts of *Brassica rapa* plants were employed. *Brassica rapa* leaf extracts contain abundant phytochemicals like kaempferol, isorhamnetin, quercetin glycosides, phenylpropanoid derivatives, indole alkaloids, sterol glucosides, and isorhamnetin glycosylated acylated with different hydroxycinnamic [17,18]. This plant extract has also been used for a number of nanoparticles (NPs)/(NCs) [16–18].

The objective of this study is to prepare a ZrO_2 - $CdWO_4$ heterojunction (type I) NC using a *Brassica rapa* leaf extract. In this study, water-splitting photocatalytic activity has been explored by developing a heterojunction between ZrO_2 and $CdWO_4$.

It is worth noting here that Cd is a toxic element, but its toxicity can be greatly reduced in the form of NC such as $CdWO_4$. Notably, ZrO_2 is a ceramic material that may further provide stability and strength to the composed NC, due to which the toxicity of Cd can be completely reduced. That is why ZrO_2 is combined with $CdWO_4$ in this study (as a type I heterojunction) to demonstrate the novelty of this material.

2. Materials and Methods

2.1. Materials

Leaves of *Brassica rapa* were collected from the general supermarket store, Jazan, KSA. In terms of precursor chemicals, cadmium iodide, A.R (Mol. wt. = 366.21), was procured from HI Media laboratory limited, Mumbai, India; purified sodium tungstate dihydrate (Mol. wt. = 329.86 g/mol) and zirconium dioxide 97% (Mol. wt. = 123.22 g/mol) were purchased from Merck Ltd., Germany. All these chemicals were of analytical grade and used without any kind of purification.

2.2. Methods

Among various preparation methods, the bioprecipitation method is considered to be a sustainable process. Plant extracts may be used in the bioprecipitation method [17]. Plant extracts contain phytochemicals, which act as reducing agents, capping agents, and functionalizing agents in NP formation [16,17]. Plant extracts are cheap, natural, and zero toxicity reagents that are easily available. As such, the NPs made through this process are less toxic, cheaper, and environmentally benign. That is why this process was given priority in this study and it was used in preparing the current photocatalyst.

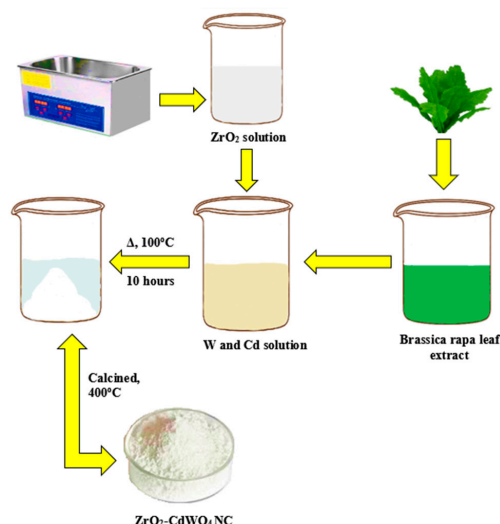
2.2.1. Preparation of *Brassica rapa* Leaf Extract

The *Brassica rapa* leaves were washed several times with distilled water, and then ground to a thick paste using a mixer grinder (Blender, Model 24CB10C, Waring Commercial, Stamford, CT, USA). An amount of 10 g of the fresh leaf paste was dispersed in 100 mL of distilled

water and heated at 70 °C for 40 min. The prepared extract was then filtered by Whatman paper No. 1, and the obtained filtrate was placed into the refrigerator for further use.

2.2.2. Synthesis of the $\text{ZrO}_2\text{-CdWO}_4$ NC

A previous study by Fatima et al. [17] was followed to synthesize a $\text{ZrO}_2\text{-CdWO}_4$ NC. The $\text{ZrO}_2\text{-CdWO}_4$ NC was prepared by taking 150 mL of 0.2 M (9.8958 g) sodium tungstate dihydrate solution and 50 mL of 0.2 M (3.6621 g) cadmium iodide solutions separately, which were later brought together, homogeneously. Thereafter, 30 mL of *Brassica rapa* leaf extract was added to the above solution and mixed thoroughly. A volume of 50 mL was taken out separately from a stock solution and 50 mL of 0.02 M (0.1232 g) of zirconium dioxide (ZrO_2) solution (which had been previously sonicated) was added under continuous stirring on a magnetic stirrer at 650 rpm to obtain the dispersed solution. The solution mixture was further stirred for 30 min, then heated at 100 °C for 10 h. The sample was then separated out by centrifuging it for 15 min at 8000 rpm, washed several times with distilled water, followed by ethanol, and then dried in an oven at 80 °C for 6 h. Thereafter, the dried sample was calcined in a muffle furnace at 400 °C for 2 h [17] as shown in Scheme 1. The yield of the sample was estimated to be approximately 2.5 g.



Scheme 1. Flow chart of the synthesis of the $\text{ZrO}_2\text{-CdWO}_4$ NC.

2.3. Characterization

The UV–Vis spectrum was recorded on a UV–Vis–NIR spectrophotometer (UV-3600-DRS spectrophotometer, Shimadzu Corporation, Kyoto, Japan). Band gap energy was calculated from a Tauc plot from the data obtained from the UV–Visible absorption spectrum of the solid sample using a Shimadzu, Kyoto, Japan UV/Vis-3600, spectrophotometer in the range of 200–800 nm. The FTIR spectrum was recorded with a Perkin Elmer-USA in the wavenumber range of 4000–400 cm^{-1} . The powder X-ray diffraction patterns were recorded on Philips PW-3710 diffractometer using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$), a Cu-filter, 35 kV generator voltage, 30 mA current, and a proportional counter detector. The SEM micrographs of the samples were obtained using a scanning electron microscope (Model: JEOL/EO-JSM-6510, Tokyo, Japan). Transmission electron microscopy (TEM) images were obtained using a JEOL HRTEM, JEM-2100F-Tokyo, Japan transmission electron microscope and were analyzed at 200 kV. Diluted samples were placed on copper grids and analyzed at 200 kV of tension. The N_2 physisorption analysis of the sample was performed using a Micromeritics Tristar 2000 instrument. The sample was degassed under helium gas at 300 °C for 2 h prior to analysis. The photoluminescence (PL) spectra of the samples were measured using a fluorescence spectrophotometer (F-4500, Hitachi, Tokyo, Japan).

2.4. H₂ Production Experiment

The photocatalytic H₂ production experiments were performed in a photochemical reactor connected with a GC instrument. The reactor was a tightly closed glass reactor (total volume of 1000 mL) equipped with a cold-water circulation pump to reduce the heat generated during the photocatalytic reaction process. For each photocatalytic experiment, 100 mg of the synthesized catalyst powder was dispersed in a mixed solution of 400 mL DI water and sacrificial reagent (20 vol. % of methanol). Then, the solution was transferred into the reactor and purged with argon gas for 30 min in order to flush all the atmospheric gases. The empty headspace was kept constant at 500 mL for all reactions. When all gases were completely purged, the reactor was irradiated using a 300 W Xenon arc lamp (provided a flux of $\sim 125 \text{ mW cm}^{-2}$ for 2 h) without any UV cutoff filter. The amount of H₂ from the reaction was determined by flowing argon as a gas carrier through the reactor in order to carry the generated gases for gas chromatography analysis (GC-1000). The measurement was performed every 30 min at a 5 h span of photoreaction.

3. Results

3.1. UV–Visible Spectroscopy

For observing the formation of NPs, optical absorption measurements are the first step. Figure 1a shows the UV-DRS spectra of ZrO₂, CdWO₄, and ZrO₂-CdWO₄. Pure ZrO₂ and pure CdWO₄ have an absorption edge at 228 nm nanoparticles and 255 nm nanorods, respectively, while the ZrO₂-CdWO₄ NC occurs at approximately 240 nm. The absorption band corresponding to these nanorods gets blue-shifted on ZrO₂ doping. The shift of the absorption band towards a shorter wavelength indicates a decrease in particle diameter and the narrowing of the band gap. The narrowing of the band gap could also be due to many interactions on the ZrO₂ deposition and the making of a heterojunction between ZrO₂ and CdWO₄. Here, the optical absorption changes mainly owing to the coupled semiconductor system following the deposition of ZrO₂ on CdWO₄ nanorods.

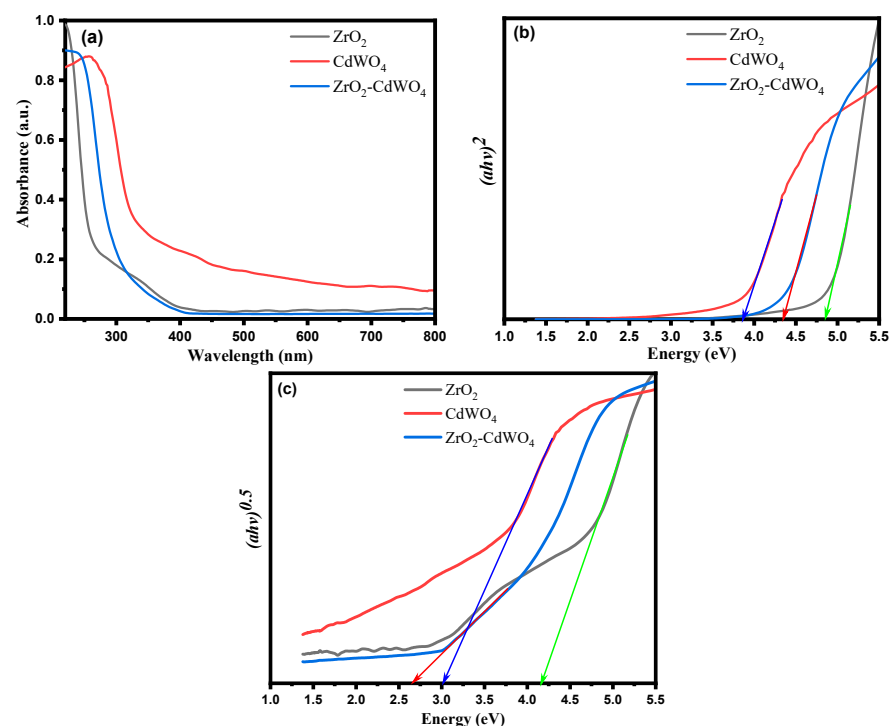


Figure 1. (a) UV–Visible diffuse absorbance spectrum of (a) ZrO₂, CdWO₄, ZrO₂-CdWO₄; (b) a Tauc plot of ZrO₂, CdWO₄, and ZrO₂-CdWO₄ as an indirect band gap; and (c) a Tauc plot of ZrO₂, CdWO₄, and ZrO₂-CdWO₄ as a direct band gap.

The UV absorption spectrum (Figure 1a) of the sample was recorded for measuring the direct and indirect bandgap of the ZrO_2 , CdWO_4 , and the ZrO_2 - CdWO_4 NC using the Tauc relation, Equation (1) [16–18]:

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g) \quad (1)$$

where A is a proportionality constant, $h\nu$ is the incident photon energy, α is the molar extinction coefficient, E_g is the bandgap of the sample, and n is the exponent to evaluate the type of electronic transition causing the absorption, which has values of $\frac{1}{2}$ and 2 for direct and indirect band gap transitions, respectively. The bandgap was determined from the Tauc plot [16–18,33]. In the Tauc plot, the intercept of the linear portion of the $(\alpha h\nu)^2$ vs. $h\nu$ on the x-axis is shown in Figure 1b and $(\alpha h\nu)^{1/2}$ vs. $h\nu$ is shown in Figure 1c. The bandgap values for ZrO_2 , CdWO_4 and the ZrO_2 - CdWO_4 NC are given in Table 1. The decrease in the band gap suggests the successful coupling of ZrO_2 to CdWO_4 .

Table 1. Comparative table for different NP/NC sizes and band gap.

Order	NPs/NCs	Preparation Method	Size of Particles (nm)	Band Gap (eV)	Ref.
1.	CdWO_4	Green synthesis using <i>Brassica rapa</i> leave extract	26–32	4.0	[34]
2.	CuO-CdWO_4	Green synthesis using <i>Brassica rapa</i> leave extract	-	2.56	[16]
3.	ZnO-CdWO_4	Green synthesis using <i>Lemon</i> extract	10–50	3.12	[17]
4.	CuO-ZnO- CdWO_4	Green synthesis using <i>Brassica rapa</i> leave extract	28–62	3.13	[18]
5.	ZrO_2	Green synthesis using <i>Sapindus mukorossi</i> plant extract	5–10	5.5	[21]
6.	CdWO_4	Green synthesis using <i>Brassica rapa</i> leave extract	-	3.06	[This study]
7.	ZrO_2 - CdWO_4	Green synthesis using <i>Brassica rapa</i> leave extract	16–29	2.66	

The band gap of the present ZrO_2 - CdWO_4 NC was determined as narrower than that of previously reported CdWO_4 -based NCs such as ZnO-CdWO_4 , CuO-CdWO_4 , and ZnO-CuO-CdWO_4 , as shown in Table 1.

Apart from the preparation method, the band gap also depends on many other factors, such as plant extract, calcination temperature, and coupled semiconductors.

Using estimated band gaps (E_g) and electronegativity (X) of conjugated semiconductors (ZrO_2 and CdWO_4), the bands (valence band, VB) and the conduction band, (CB) edge position (E_{VB} and E_{CB}) of the current photocatalyst were determined by applying Equation (2) [16], the result of which is given in Table 2.

$$E_{VB} = X - E_e + 0.5E_g, E_{CB} = E_{VB} - E_g \quad (2)$$

Table 2. Band edge position in ZrO_2 - CdWO_4 heterojunction.

Semiconductors	E_g (eV)	X (eV)	E_{VB} (eV)	E_{CB} (eV)
ZrO_2	4.16	5.91	3.49	−0.67
CdWO_4	3.06	6.28	3.31	0.25

Here, E_e is the energy of free electrons, which is ~4.5 eV.

Using the edge positions of these bands (VB and CB), the heterojunction design was proposed as type I [19]. Type I heterojunctions aid charge separation and prevention of electron-hole recombination.

3.2. FT-IR Analysis

The infrared spectrum of the $\text{ZrO}_2\text{-CdWO}_4$ NC (Figure 2) showed a broad-spectrum peak at approximately 3429.5 cm^{-1} , contributing to the stretching vibrations of the O–H bond [35]. The peaks that appeared at approximately 2919 and 2854.1 cm^{-1} are for the stretching vibration of the C–H bond coming from the *Brassica rapa* leaf extract [36]. A sharp peak at 1633.6 cm^{-1} was assigned for the bending vibration of Zr–OH and adsorbed moisture content [33]. The absorption peaks at 1020.7 and 829.3 cm^{-1} in the sample are assigned for the –OH group and for the vibration of the Zr–O bond, confirming that ZrO_2 is present in the sample [37]. The sharp peaks at 890.0 cm^{-1} , 717.6 cm^{-1} , 587.96 cm^{-1} , 412.3 cm^{-1} and 412 cm^{-1} correspond to Cd–O stretching vibrations of Cd–O–W, stretching vibrations of the W–O–W bond in the WO_4^{2-} group and in-plane deformation of the WO_4^{2-} group [16–18,37–40].

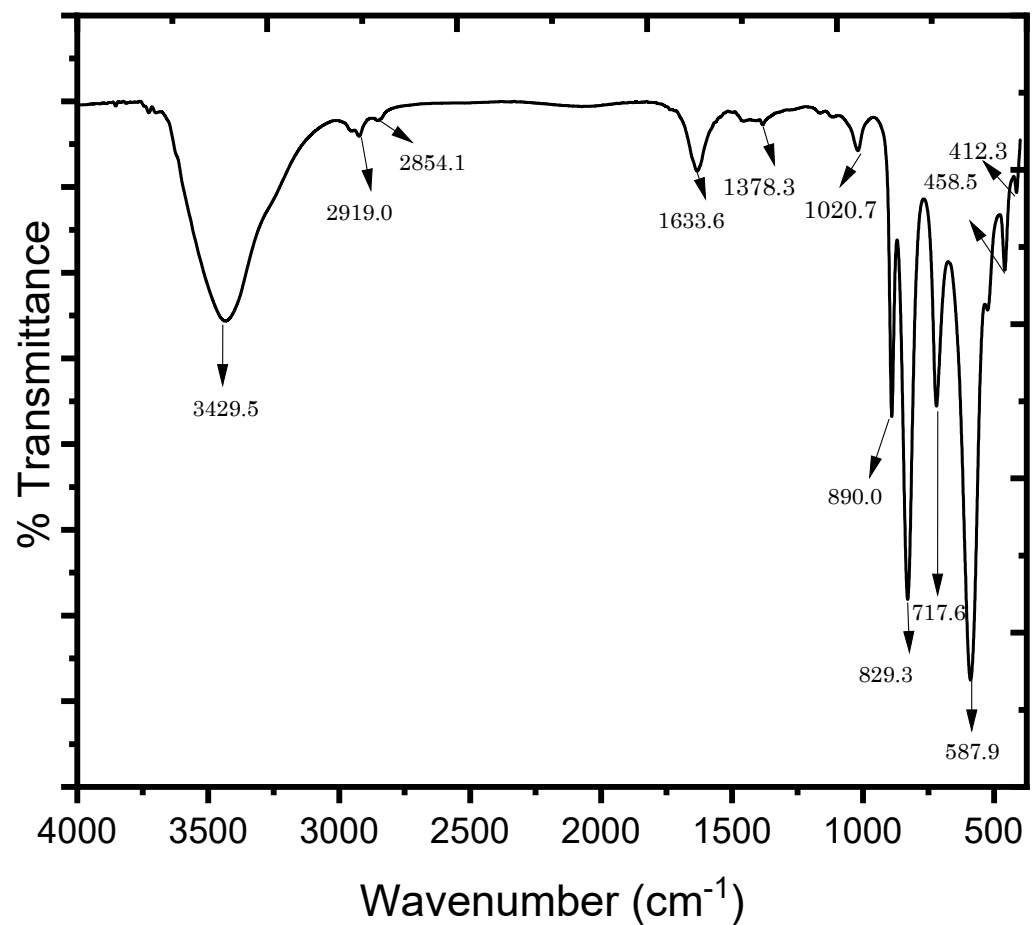


Figure 2. FT-IR spectra of the $\text{ZrO}_2\text{-CdWO}_4$ NC.

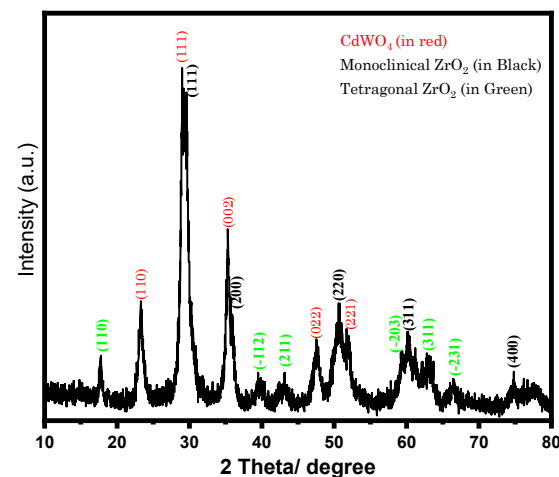
The FT-IR spectrum of the current $\text{ZrO}_2\text{-CdWO}_4$ NC can be verified with the FT-IR spectrum of the previously reported NC based on CdWO_4 prepared using plant extracts (Table 3). The current nanocomposite showed an almost identical FTIR spectrum to the previous one, confirming the validation of the present analysis. The presence of typical peaks corresponding to the plant extracts (*Brassica rapa* leaf) as well as the nanomaterial ($\text{ZrO}_2\text{-CdWO}_4$), which is consistent with the previous study, suggest the preparation of the $\text{ZrO}_2\text{-CdWO}_4$ NC that was chemically functionalized with phytochemicals from the plant extract. These functional groups can aid light absorption as suggested in the previous study.

Table 3. Comparative FTIR analysis of various CdWO₄ NP-based composites prepared using plant extracts.

Order	NCs	Plant Extract	FTIR Peaks		Ref.
			Vibrational Frequencies of Functional Groups due to Plant Extract	Vibrational Frequencies of M-O Due to NPs	
1.	CdWO ₄	<i>Brassica rapa</i> leaf	3419 cm ⁻¹ -O-H; 2923 cm ⁻¹ and 2853 cm ⁻¹ C-H of CH ₃ , and CH ₂ ; 1460–1020 cm ⁻¹ aromatic C-C and C-O, respectively	900–500 cm ⁻¹ Intrinsic vibrations of CdWO ₄	[34]
2.	ZnO-CdWO ₄	<i>Lemon</i> leaf	3459 cm ⁻¹ -OH; 1671 cm ⁻¹ -O-H/amide; 1469 cm ⁻¹ -C-H; 1084 cm ⁻¹ C-N	844 cm ⁻¹ W-O-W bond in the WO ₄ ; 586 cm ⁻¹ Cd-O; 447 cm ⁻¹ and 417 cm ⁻¹ Zn-O	[17]
3.	CuO-CdWO ₄	<i>Brassica rapa</i> leaf	3481–3400 cm ⁻¹ -O-H; 1670–1590 cm ⁻¹ C = O, -NH, and aromatic C = C; 1460–1020 cm ⁻¹ aromatic C-C and C-O, respectively	1000–400 cm ⁻¹ CuO and CdWO ₄	[16]
4.	CuO-ZnO-CdWO ₄	<i>Brassica rapa</i> leaf	3664–3060 cm ⁻¹ O-H; 2924 and 2854 cm ⁻¹ C-H of CH ₃ and CH ₂ ; 1746 and 1634 cm ⁻¹ -C = O and -O-H	836 cm ⁻¹ Cd-O-W; 708 cm ⁻¹ W-O; 450 cm ⁻¹ Cd-O; 531 cm ⁻¹ and 595 cm ⁻¹ Zn-O and Cu-O, respectively	[18]
5.	ZrO ₂ -CdWO ₄	<i>Brassica rapa</i> leaf	3429 cm ⁻¹ O-H; 2919 and 2854 cm ⁻¹ C-H of CH ₃ and CH ₂ ; 1633 cm ⁻¹ Zr-OH	829 cm ⁻¹ Zr-O; 890.0 cm ⁻¹ , 717.6 cm ⁻¹ and (587.96 cm ⁻¹ and 412.3 cm ⁻¹ and 412 cm ⁻¹) Cd-O-W, W-O-W bond in WO ₄ ²⁻ group and in-plane deformation of the WO ₄ ²⁻ group	[This study]

3.3. XRD Analysis

Figure 3 shows the XRD pattern of the ZrO₂-CdWO₄ NC within the 2 θ range of 10–80°. XRD analysis was conducted using the Crystal Impact Match program. Results obtained confirmed that CdWO₄ has monoclinic symmetry with cell dimensions of $a = 4.9750 \text{ \AA}$, $b = 5.7650 \text{ \AA}$, $c = 5.0370 \text{ \AA}$ and $\beta = 91.840^\circ$ (space group P 1 2/c 1) and ZrO₂ has tetragonal symmetry with cell dimensions $a = 3.6120 \text{ \AA}$ and $c = 5.2120 \text{ \AA}$ (space group P 42/n m c). The 2 θ values at 23.26°, 28.83°, 35.49°, 47.44°, and 51.93° corresponded to (110), (111), (002), (022), and (221) lattice planes, indicating a wolframite structure of CdWO₄ (entry number 969013916) [17,39,40]. The 2 θ values at 29.10°, 50.55°, 60.21°, and 63.14° correspond to the tetragonal phase of ZrO₂ (entry number 961526428) [41,42]. The amount of CdWO₄ and ZrO₂ in samples is 90.2% and 9.8%, respectively. The XRD pattern of ZrO₂-CdWO₄ can also be verified from the XRD spectrum of the previously reported CdWO₄-based NC such as ZnO-CdWO₄, CuO-CdWO₄, and CuO-ZnO-CdWO₄. The X-ray diffraction (XRD) pattern of the ZrO₂-CdWO₄ nanocomposite showed distinct peaks that corresponded to the crystal facets of the monoclinic phase of ZrO₂, specifically (111), (200), (220), (311), and (400). These results were consistent with the crystal structure identified by JCPDS no. 00–037-1484. Furthermore, the ZrO₂-CdWO₄ NC exhibited diffraction peaks that were identified as the crystal facets (110), (−112), (211), (−203), (311), and (−231) of the tetragonal phase of ZrO₂ (JCPDS # 00–017-0923). The X-ray diffraction (XRD) pattern of ZrO₂-CdWO₄ nanocrystals indicates the presence of ZrO₂ in both the monoclinic and tetragonal phases.

**Figure 3.** X-ray diffraction pattern for the ZrO₂-CdWO₄ NCs.

The crystallite size was calculated using Scherrer's Equation (3) [17]:

$$D = K\lambda / \beta \cos \theta \quad (3)$$

where D is the crystallite size, constant $K = 0.94$, λ is the X-ray wavelength of Cu $K\alpha$ radiation (1.54 Å), and β is the full width at half maximum (FWHM). The average crystallite size corresponding to the highest peaks of ZrO_2 and $CdWO_4$ was determined as ~8 nm and ~26 nm, respectively.

3.4. SEM Analysis

Particles were in an aggregated state. Aggregation of particles occurred due to van der Waal forces of attraction between them (Figure 4a). The average diameter of the ZrO_2 - $CdWO_4$ NC increased due to the presence of ZrO_2 . The EDAX pattern of the ZrO_2 - $CdWO_4$ NC is shown. The composition of the sample shows the presence of the zirconium, oxygen, cadmium, and tungsten elements. The contents of Zr, O, Cd, and W are 5.74 wt%, 21.99 wt%, 27.65 wt%, and 44.62 wt% (Figure 4b). Also, the spectral peaks reveal the presence of Zr and O at 2.05 and 0.5Kev, respectively, which confirms the presence of Zr and O in $CdWO_4$ nanorods.

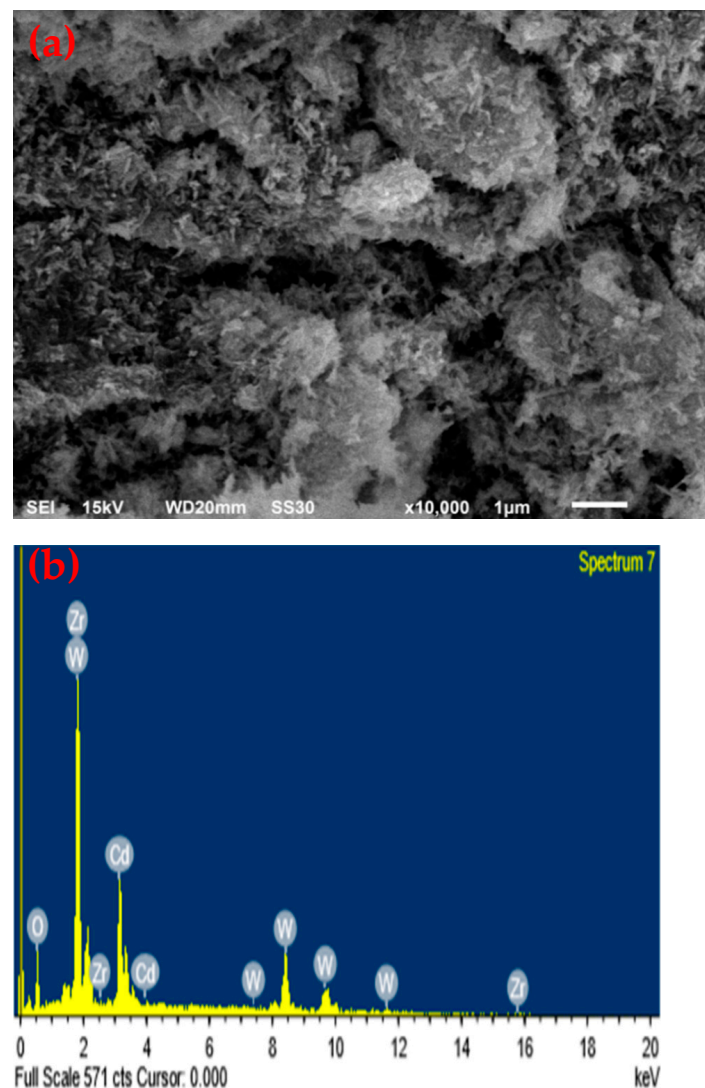


Figure 4. (a) SEM images and (b) EDX of ZrO_2 - $CdWO_4$ NC.

3.5. TEM Analysis

The particle size, pattern, morphology, and distribution of crystallite were confirmed by transmission electron microscopy. TEM images of the biogenically synthesized $\text{ZrO}_2\text{-CdWO}_4$ NC at 400°C of calcination are given in Figure 5. The presence of ZrO_2 on the rod-shaped CdWO_4 nanorods increases the roughness. Further, the particles were well crystallized without defects and self-aggregated. Self-aggregation is caused by the high generation rate of CdWO_4 nanorods. Due to fewer electron density differences between the particles, the ZrO_2 particles and CdWO_4 nanorods appeared to be slightly different in color. The particle size diameter is nearly 16–30 nm. The nanorods CdWO_4 in NC can also be verified from the TEM images of previously reported CdWO_4 -based NCs such as ZnO-CdWO_4 , CuO-CdWO_4 , and CuO-ZnO-CdWO_4 .

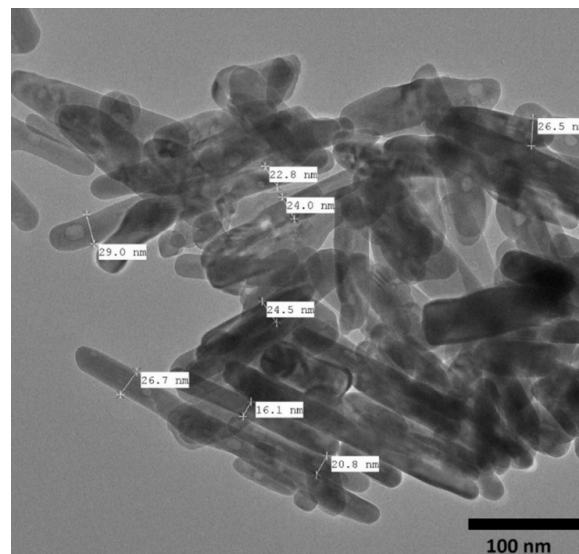


Figure 5. TEM images of the $\text{ZrO}_2\text{-CdWO}_4$ NC.

3.6. Nitrogen Adsorption–Desorption Isotherm Analysis

In the present study, nitrogen (N_2) absorption and desorption analysis of $\text{ZrO}_2\text{-CdWO}_4$ were also studied, the result of which is seen in Figure 6. This analysis gives the information about the surface area and pore size of the prepared sample. Figure 6 reveals the type III adsorption isotherm, which gave a surface area of $\text{ZrO}_2\text{-CdWO}_4$ of $19.6\text{ m}^2/\text{g}$. The pore volume and half pore width of the prepared sample were estimated as 0.0254 cc/g and $9.457\text{ \AA}$, respectively.

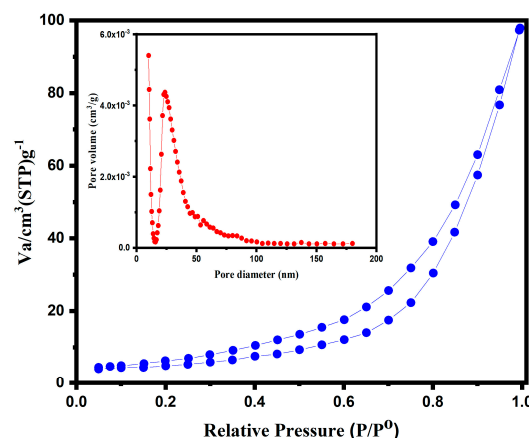


Figure 6. Nitrogen adsorption–desorption isotherm (inset pore diameter distribution) of the $\text{ZrO}_2\text{-CdWO}_4$ NC.

3.7. Photoluminescence Analysis

To elucidate the photogenerated charge carrier separation at the interface of ZrO_2 - CdWO_4 , photoluminescence (PL) spectra were analyzed. The PL spectrum shows the comparative e^- - h^+ recombination rate in the bare semiconductors and heterojunction [16]. Figure 7 shows the PL spectra of ZrO_2 and CdWO_4 , and also the heterojunction (ZrO_2 - CdWO_4). As can be seen in the PL spectra, the PL intensity was significantly reduced when the heterojunction was formed as compared to ZrO_2 and CdWO_4 [15,16]. The decrease in the PL intensity upon ZrO_2 loading might be due to the decrease in the rate of e^- - h^+ recombination upon loading ZrO_2 on CdWO_4 [15,16]. Therefore, the heterojunction photocatalyst shows even better photolytic activity than the virgin ZrO_2 and CdWO_4 .

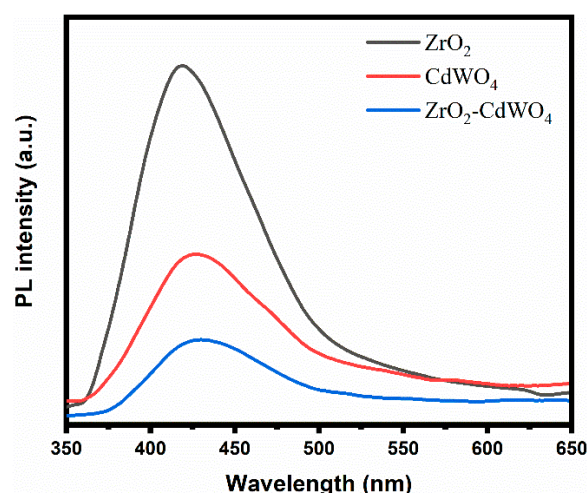


Figure 7. PL spectra of ZrO_2 , CdWO_4 , and the ZrO_2 - CdWO_4 NC.

3.8. Photocatalytic Performance Results

As reported in previous studies, these catalysts exhibit better H_2 production activity in the presence of a sacrificial agent than a virgin photocatalyst. It is well known that the amount of protons, i.e., H^+ ions, for H_2 production in the presence of a sacrificial agent increases. The sacrificial agent provides H^+ ions, which are responsible for increased photocatalyst activity and water splitting. In this study, methanol was used as a sacrificial agent and it was found that this sacrificial agent increases the rate of H_2 production. The increased H_2 production rates with sacrificial agents can be easily seen in Figure 8a.

A systematic study of the photocatalytic activity of the ZrO_2 - CdWO_4 NC was performed for H_2 production via water splitting with the sacrificial agent (methanol). H_2 production via water splitting was performed under various conditions such as different catalyst amounts, time, temperatures, and sacrificial agents.

The time effect has also been monitored for this study, and is shown in Figure 8a. Figure 8a confirms that H_2 production increases as time increases. It can be seen from Figure 8b that the H_2 production rate increases as the photocatalyst is added. The point is that the number of surface sites increases with the increase in photocatalyst concentration (facilitates visible light absorption), due to which the catalytic activity of the catalyst also increases. This is because the rate of H_2 production showed a marked increase when increasing the concentration of the photocatalyst prepared in this study. As can be seen, the concentration of the photocatalyst ranged from 25 mg to 250 mg, and H_2 production ranged from 165 $\mu\text{mol/g}$ to 1574 $\mu\text{mol/g}$.

Figure 8c shows the temperature effect on water splitting. The increased temperature facilitates the easy excitation of electrons from VB to CB, charge separation, and prevention of e^- - h^+ recombination, which is responsible for enhanced water splitting. In addition, the temperature increase reduces the viscosity of water, which is also responsible for water

splitting. Different pH effects were also measured for H₂ production efficiency, as shown in Figure 8d, and pH 7.0 was observed as the optimum pH for good H₂ production.

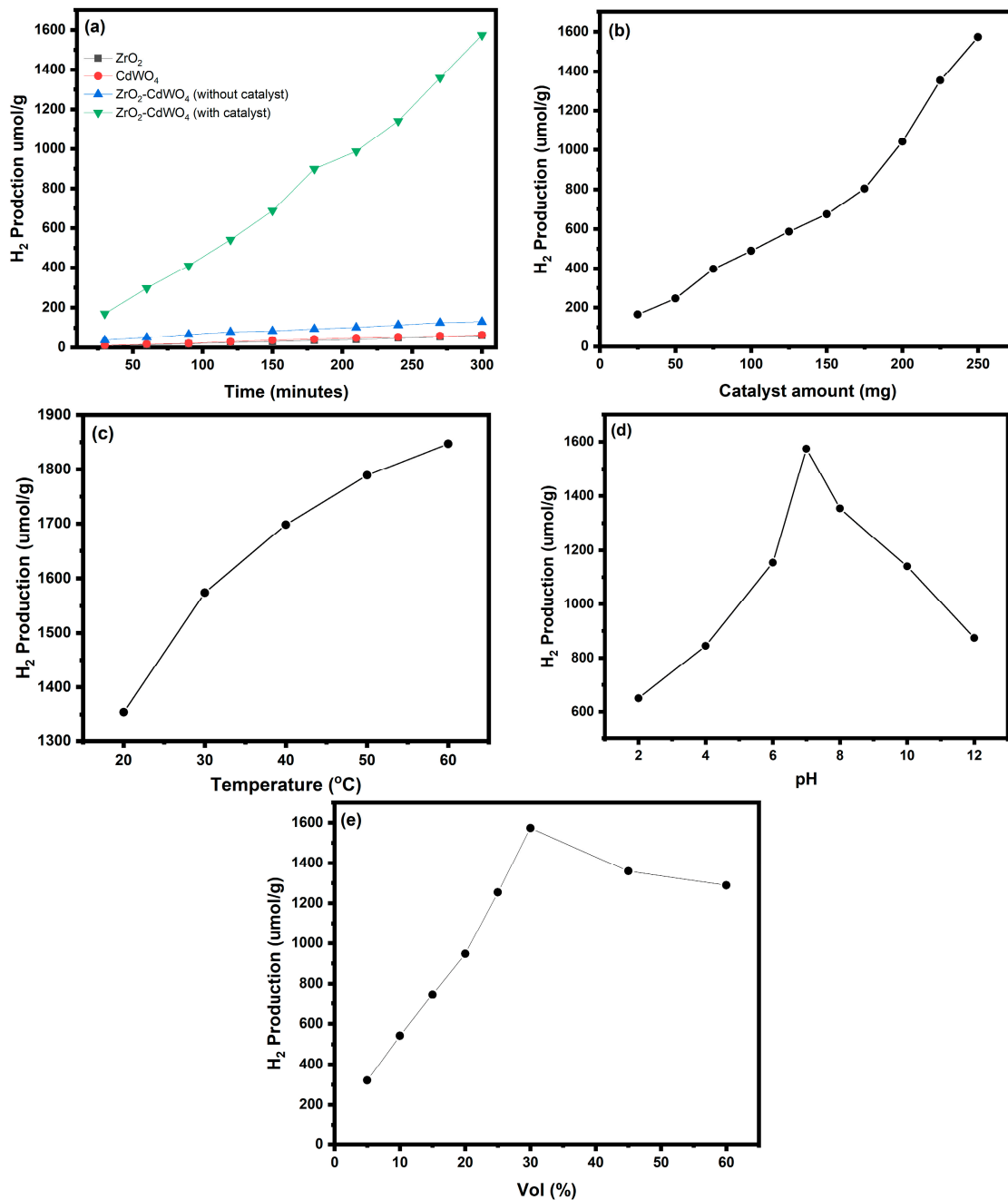
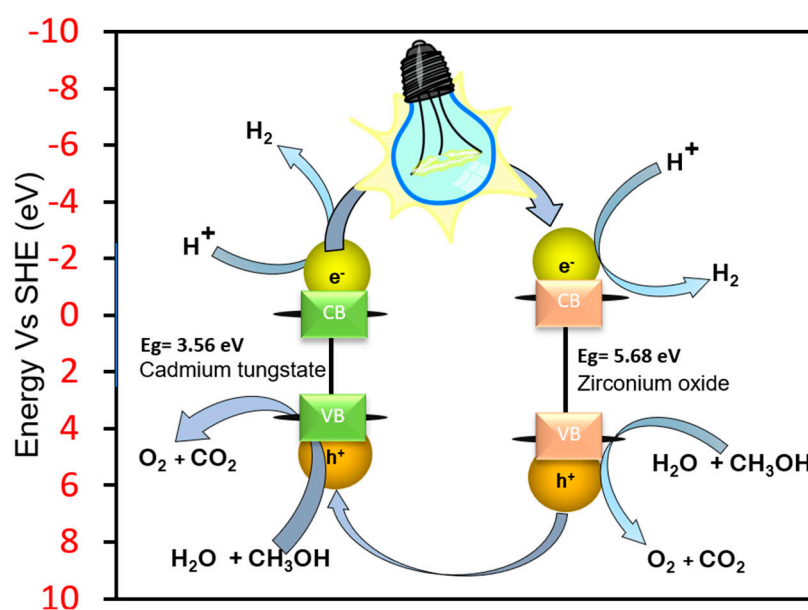


Figure 8. Optimization results of H₂ production via water splitting using ZrO₂-CdWO₄: (a) time effect, (b) catalyst amount effect, (c) temperature effect, (d) pH effect, and (e) MeOH vol% effect.

The effect of MeOH (sacrificial agent) concentration on H₂ production via water splitting was also observed. As shown in Figure 8e, H₂ production initially increases with an increase in the concentration of MeOH, and the H₂ production rate decreases. The reason behind the decrease in the H₂ production rate might be the blocking of the surface site on the high loading of MeOH. The blocking of surface sites may eventually decrease the visible light absorption for photocatalytic activity.

3.9. The Mechanism Involved

A heterojunction photocatalyst was used in this study. According to previous studies, heterojunction photocatalysts can be arranged in a variety of ways depending on the band edge positions of their constituent semiconductors, including dominant straddling gap (type I), staggered gap (type II) or broken gap (type III) heterojunction photocatalysts [19]. The present heterojunction photocatalyst was made up of two separate semiconductor units (ZrO_2 and CdWO_4) whose band (VB and CB) positions are different to each other. According to their band edge positions, the ZrO_2 - CdWO_4 semiconductor interface can be arranged as a straddling gap (type I) heterojunction. A Schottky barrier is formed due to different band positions or type I arrangement of the heterojunction (suggested by UV-DRS and PL spectra). Therefore, the possibility of migration of e^- to the catalyst surface is increased via charge separation, and prevention of e^- - h^+ recombination, as shown in Scheme 2 [16,18].



Scheme 2. Plausible reaction mechanism for H_2 production over ZrO_2 - CdWO_4 .

When visible light falls on such a heterojunction photocatalyst, a valence band (VB) e^- can be excited from one of the units (either ZrO_2 or CdWO_4) and move to the conduction band (CB) of that unit, leading to the formation of h^+ in VB. Due to the difference in the positions of the bands (VB and CB) in such units (ZrO_2 and CdWO_4) of the developed heterojunction, the possibility of migration of e^- and h^+ from one unit to the other unit may increase. This way, the excited e^- and h^+ do not go back and can rapidly and continuously transfer from one unit (ZrO_2) to the other unit (CdWO_4) of the semiconductor, thus causing charge separation, and also preventing charge recombination.

Due to this charge separation and prevention of charge recombination, the electronic charge becomes distributed over the entire surface of the heterojunction photocatalyst. In such a situation, the e^- and h^+ reach the surface of the catalyst and react with water, split the water, and produce H_2 gas. Because, in this study, a sacrificial agent such as MeOH has been used, the MeOH acts as a proton source and therefore increases the photocatalytic activity occurring in the presence of these extra protons. Based on the theory presented in the present study, the speculated mechanism has been shown through Scheme 2 [16]. Our group [43,44] has previously reported the use of $\text{Pt-Ag}/\text{Ag}_3\text{PO}_4\text{-WO}_3$ NCs for photocatalytic H_2 production from bioethanol.

3.10. The Reusability Study

It is very important to assess the stability and life cycle of the photocatalyst for cheap and smooth production of H₂ gas. In view of this, the photocatalyst used in this study was also used for several cycles. To investigate the reuse activity of the catalyst, an experiment was conducted with 250 mg of ZrO₂-CdWO₄ at room temperature (27 °C) and 30 vol% methanol. The catalyst used in each cycle is separated by centrifuging and then washed with deionized water and dried, which was reused. The results of this experiment are shown in Figure 9, which makes it clear that even after 7 cycles, the present catalyst showed excellent H₂ production activity. The present catalyst retained 75% of its activity even after 7 cycles. The 25% drop in activity may be due to a reduction in catalyst weight and a reduction in surface activity. It is also worth noting here that this catalyst displayed almost no activity in the absence of a sacrificial agent.

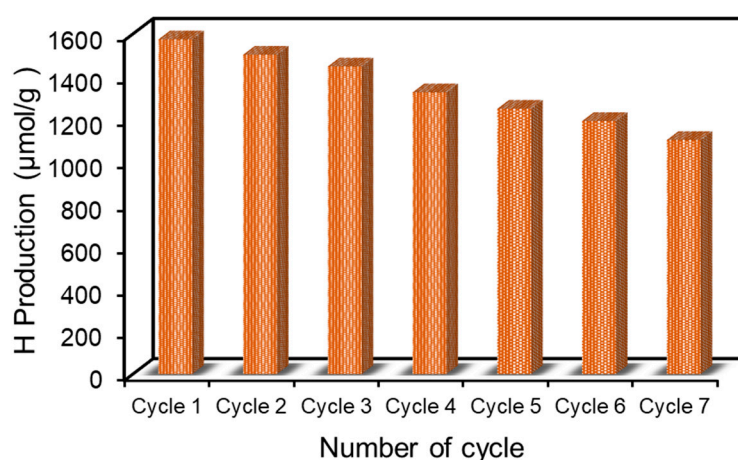


Figure 9. Reutilization of ZrO₂-CdWO₄ for H₂ production.

3.11. Comparative Analysis

A comparative study was conducted for this study. First, the photocatalyst was compared with its virgin version of NPs. The versions of NPs here are ZrO₂ and CdWO₄. The photocatalytic activity of both these NPs for water splitting was observed and it was found that both these versions of the nano-catalysts showed lower H₂ production rates as compared to the heterojunction photocatalyst (ZrO₂-CdWO₄). The low efficiency of these virgin nano-photocatalysts may be due to the low charge separation and fast electron-hole recombination between VB and CB, whereas a heterojunction photocatalyst is a junction that is formed when zirconium oxide and cadmium tungstate are mixed and it can prevent electron-hole recombination; therefore, this photocatalyst is responsible for the increased H₂ production rate (Figure 8a).

The present photocatalyst was also compared with several previous photocatalysts and it can be seen from Table 4 that the present photocatalyst has shown comparable performance to the previous photocatalyst and has also shown improved results. This suggests that the existing photocatalyst is a better catalyst for H₂ production.

Table 4. Comparative table of different nanomaterials for H₂ production.

Order	Material	Sacrificial Agent	Light Sources	H ₂ Production (μ mol/g)	Ref.
1.	CuO-CdWO ₄	MeOH	Sunlight	~1600	[16]
2.	TiO ₂ /ACS	Glycerine	Sunlight	203	[34]
3.	Pt-Cu-TiO ₂	MeOH	LED irradiation	~2384	[45]
4.	Pt/TiO ₂	MeOH	Sunlight	195.5	[46]
5.	ZrO ₂ -CdWO ₄	MeOH	Sunlight	1574	This study

However, comparing photocatalysts in terms of their H₂ production capacity would be a biased analysis as the performance parameters and conditions differed for each reported catalyst. Many photocatalysts are given in Table 4; most of these catalysts were made through the chemical method; in comparison, the present catalyst has been made through the precipitation method, which makes the present catalyst cheap, low cost, and environmentally friendly. Additionally, the current photocatalyst is a type I heterojunction, which performs the water-splitting process more smoothly than other catalysts for seven reused cycles. This gives it an advantage over the other reported catalyst. Therefore, the present catalyst is better than other reported photocatalysts. Although, to validate these inferences, more concrete fundamental mechanistic studies are required.

4. Conclusions

This study describes using plant extracts to successfully prepare ZrO₂-CdWO₄, a heterojunction material. A heterojunction was made by depositing tetragonal zirconium dioxide over the monoclinic cadmium tungstate. The 2.66 eV energy band gap was reported for this photocatalyst, which was lower than the bare oxide (ZrO₂ and CdWO₄) as well as various reported CdWO₄-based nanocomposites (ZnO-CdWO₄ and CuO-ZnO-CdWO₄). A ZrO₂ heterojunction with CdWO₄ may lower the band gap energy and aid visible light photon absorption. Critically, it was reported that heterojunction formation forms a Schottky barrier, which increases charge separation and prevents electron-hole combinations. This mechanism exhibits a complete distribution of electrons on the semiconductor surface, which is important for photocatalytic applications. In this study, hydrogen production was enabled via water splitting to understand photocatalytic application. The heterojunction material resulted in improved hydrogen production. After a 5 h reaction at 27 °C, pH 7, and using 30 vol. % of methanol, 1574 µmol/g hydrogen gas was produced using 250 mg of ZrO₂-CdWO₄. This is a useful study on heterojunction materials being used for hydrogen production.

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