1. Introduction

Global energy consumption and rapid environmental pollution are serious societal concerns due to the massive use of fossil fuels such as coal, oil, and natural gas. Furthermore, the combustion of these fossil fuels causes serious environmental impacts ranging from air and water contamination to global warming. Therefore, it is high time to develop renewable clean carbon-free energy resources to control our dependence on fossil fuels. Hydrogen, which as a fuel has been attractive for hydrogen, which as a fuel has been attractive for the replacement of fossil fuels, could be an alternative energy source for solving the current energy crisis and environmental pollution. Hydrogen evolution from photocatalytic water splitting as a process of decomposition of water (H2O) using sunlight energy is an economical approach to converting solar energy into chemical energy (H2) and oxygen (O2) fuel for storage.\(^2\)\(^3\)

\[
\text{H}_2\text{O} \rightarrow \text{H}_2 + 1/2\text{O}_2; \quad \Delta G = +237 \text{ kJ mol}^{-1}
\]  

The key factors for effective photocatalysts are high visible light activity, inexpensiveness, and long-term stability. Pioneering work was done by Fujishima and Honda using TiO2 electrodes.\(^4\) In the last four decades, various semiconductors have been designed and developed for photocatalytic hydrogen generation, such as ZnO,\(^5\) Cu2O,\(^7\) Nb2O5,\(^8\) Ta2O5,\(^9\) WO3,\(^10\) CdS,\(^11\) and ZnS.\(^12\) However, binary oxide/sulfide photocatalysts have low photocatalytic efficiency due to their high resistance, unsuitable band gap, low stability, rapid electron–hole pair recombination, and photo-corrosion.\(^13\)\(^14\) Previous reports have shown that cation/anion doping in metal oxides and noble metal loading (Ag, Au, Pt, etc.) on TiO2 potentially tune the band gap and enhance absorption towards the longer wavelength. Nevertheless, the expected outcome in the activity of the photocatalyst is unremarkable because of its poor efficiency and...
mixed side products.\textsuperscript{15,16} Therefore, the development of an 
active semiconductor photocatalyst is still a great challenge for 
the scientific community. Recently, transition metal tungsstates 
of the type [MWO\textsubscript{4}] \( (M = CO, Ni, Cu, or Zn, etc.) \) have attracted 
widest interest as promising candidates owing to their 
high stability, low cost, and unique crystal structure, and these 
compounds have a broad range of applications.\textsuperscript{17,18} Among 
different tungsstates, the wolframite-type monoclinic structure 
of manganese tungstate [MnWO\textsubscript{4}] is a very promising material 
due to its suitable bandgap of 2.7 eV, which can effectively 
absorb visible light, relatively high stability, excellent reactivity, 
\textit{etc.}\textsuperscript{19} However, its photocatalytic performance is very low due to 
limited light absorption in the visible region.\textsuperscript{20} Recently, many 
efforts have been made to use MnWO\textsubscript{4} for the photocatalytic 
decomposition of organic pollutants and hydrogen generation. 
However, the photocatalytic activity of pure MnWO\textsubscript{4} is still poor 
due to the quick recombination of photogenerated electron and 
hole pairs. Moreover, electrons in the conduction band (CB) of 
MnWO\textsubscript{4} (+0.4 eV NHE) cannot reduce O\textsubscript{2} \( \text{via} \) single-electron 
processes, which greatly limits the photocatalytic performance of 
MnWO\textsubscript{4}.\textsuperscript{21,22} Therefore, the photocatalytic activity of MnWO\textsubscript{4} 
needs to be further improved for use in practical applications. 
In the past, immense work has been done in the synthesis of 
heterojunctions wherein one photocatalyst coupled with 
another catalyst is significantly beneficial to enhancing photo-
catalytic activities.\textsuperscript{23,24} Therefore, coupling MnWO\textsubscript{4} with another 
co-catalyst with matching bandgap is an ideal way to enhance 
the photocatalytic activity of MnWO\textsubscript{4}. Among different co-
catalysts, cadmium sulfide (CdS) has attracted a lot of attention 
for the construction of a heterojunction due to its narrow 
bandgap with a high CB position, which can greatly enhance the 
photocatalytic activity by effectively separating the electron– 
hole pairs, and its visible light absorption.\textsuperscript{25} Many CdS-based 
heterojunction photocatalysts have been developed so far, 
including CdS/WO\textsubscript{3},\textsuperscript{26} MoS\textsubscript{2}/CdS,\textsuperscript{27} CdS/ZnWO\textsubscript{4},\textsuperscript{28} and CdS/ 
BiWO\textsubscript{4},\textsuperscript{29} which were prepared \textit{via} different methods and showed 
enhanced photocatalytic activities. We have also reported 
CdS@CdWO\textsubscript{4},\textsuperscript{30} for hydrogen generation and pollutant degra-
dation. These hybrid multi-semiconductor Z-scheme systems 
have advantages with one semiconductor having a high CB 
minimum and the other a low VB maximum and therefore they 
can provide a large overpotential for the photocatalytic process 
and also reduce charge carrier recombination. Therefore, the 
formation of a CdS@MnWO\textsubscript{4} heterojunction can create an ideal 
photocatalyst for photocatalytic hydrogen evolution. Herein, we 
report a successful synthesis of a CdS@MnWO\textsubscript{4} heterostructure 
photocatalyst with different molar ratios through a facile 
hydrothermal method. Similarly, the as-prepared photocatalyst 
was subjected to a photocatalytic water splitting reaction for 
hydrogen generation under visible light irradiation and it shows 
a much-improved hydrogen generation rate compared to pure 
photocatalysts. In the present work, we have successfully 
synthesized a highly efficient CdS@ZnWO\textsubscript{4} heterostructure 
photocatalyst using the hydrothermal method, in which CdS 
nanoparticles are decorated on 1D MnWO\textsubscript{4} nanorods. To the 
best of our knowledge, this is the first report on CdS/MnWO\textsubscript{4} to 
describe enhanced photocatalytic activity \textit{via} Z-scheme electron 
transfer for hydrogen generation under solar light. In this work, 
the effect of CdS on the structural, optical, morphological and 
photocatalytic properties was investigated and is discussed. The 
Z-scheme mechanism of photocatalytic hydrogen from water is 
also proposed.

2. Experimental sections

Sodium tungsten oxide di-hydrates \( \text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O} \), manganese 
nitrate tetra-hydrate \( \text{Mn(NO}_3)_2 \cdot 4\text{H}_2\text{O} \), cadmium nitrate 
etrahydroxide \( \text{Cd(NO}_3)_2 \cdot 4\text{H}_2\text{O} \), and thiourea \( \text{NH}_2\text{CSNH}_2 \) used 
for the preparation of the catalyst were of analytical grade (SD 
Fine-Chem Limited, India) and used without any further 
purification.

2.1 Synthesis of MnWO\textsubscript{4} and CdS@MnWO\textsubscript{4} nanorods

In a typical synthesis, 0.05 mol of Na\textsubscript{2}WO\textsubscript{4} \cdot 2H\textsubscript{2}O and 0.05 mol 
of Mn\textsubscript{(NO}_3\textsubscript{2}) \cdot 4H\textsubscript{2}O were dissolved in 140 mL of distilled water 
and stirred for 20 min. The clear solution was then transferred 
into a 200 mL capacity Teflon autoclave and kept at 180 °C for 
24 h. After the completion of the reaction, the autoclave 
was cooled naturally. After washing several times with absolute 
éthanol and deionized water, a brownish colored powder was 
obtained. This pure sample is labeled MNW-0. Similarly, 
CdS@MnWO\textsubscript{4} composites have been synthesized by following 
the same route with the addition of 5, 10, 15, 20 M\% of 
cadmium nitrate \( \text{Cd(NO}_3)_2 \cdot 4\text{H}_2\text{O} \) and thiourea (TU) to the 
above solution. These samples have been labeled MNC-1, 2, 3, 
and 4.

2.2 Photocatalytic study

2.2.1 Photocatalytic hydrogen generation from water.

Photocatalytic hydrogen generation was carried out through 
water splitting at room temperature under sunlight with 0.1 g of 
each photocatalyst sample suspended in 100 mL of double 
distilled water and Na\textsubscript{2}S/Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} as a sacrificial reagent in the 
reactor system. Pure MnWO\textsubscript{4} and MNW photocatalysts were added with 0.5 wt\% preloaded platinum as a co-catalyst. Argon 
gas was purged through this reaction mixture to remove the 
dissolved gases. The 250 mL round bottom flask was connected 
to a graduated measuring gas collector tube. The gas collector 
tube had a septum arrangement to get rid of the evolved gas 
through a gas-tight syringe and to measure the amount of gas 
evolved. The amount of gas evolved was noted over time. The 
purity of the collected gas was analyzed using gas chromatog-
raphy (Model Shimadzu GC-14B, MS-5 Å column, TCD, Ar 
carrier).

2.2 Sample characterization

The as-synthesized powders were analyzed to determine their 
phase purity and crystalline structure by using the X-ray 
diffraction (XRD) technique (Advance, Bruker AXS D8) using 
Cu K\textsubscript{α}1 \((1.5406 \text{ Å})\) radiation. The bandgap of the samples was 
determined by using a UV-VIS spectrophotometer (Perkin-
Elmer) in the range of 300–800 nm. Morphological studies 
and crystallinity analysis were carried out using high-resolution
transmission electron microscopy (HRTEM Philips EM-CM-12) operated at an accelerating voltage of 200 kV. The photoluminescence (PL) spectra were recorded using an F-3 fluorescence spectrophotometer (Horiba Jobin Yvon).

3. Results and discussions

3.1 Structural study

The crystal structure and phase formation of the as-synthesized MnWO$_4$ (MNW-0) and CdS@MnWO$_4$ nanocomposites (MNC-1, 2, 3, and 4) were determined by powder XRD (Fig. 1). Fig. 1 shows well-indexed diffraction peaks of MNW-0, indicating single-phase formation of a MnWO$_4$ monoclinic structure of wolframite-type, matching the reported values (JCPDS card no 015-0774). All the reflection peaks were indexed with lattice parameters $a = 4.80$ Å, $b = 5.71$ Å, $c = 4.97$ Å and $\beta = 91.22^\circ$ (space group $P2_1/c$, with $Z = 2$). In the case of CdS@MnWO$_4$ composites (MNW-1–4), small additional peaks are observed with the co-existence of both MNW and CdS phases without any trace of other impurities, demonstrating the successful formation of the CdS@MnWO$_4$ composite material. The three main diffraction peaks are located at $2\theta = 24.79^\circ$, $26.42^\circ$, and $28.22^\circ$, corresponding to crystal diffraction planes of (1 0 0), (0 0 2), and (1 0 1), respectively, of the hexagonal phase of CdS, matching well with JCPDS card no 06-0314, and labeled by vertical red dashed lines in Fig. 1. Furthermore, the intensity of the CdS peaks is less sharp than that of MNW, due to the lower concentration of CdS compared to pure MnWO$_4$. Furthermore, the intensity of the CdS peaks increases as the CdS concentration increases.

Overall, the CdS@MnWO$_4$ samples with different CdS amounts show slight declines in the peaks observed in sample MNC-4 at 29.9, 36.04, 40.02$^\circ$. The decrease in peak intensity of MnWO$_4$ is due to its low crystallization due to higher CdS content, which suppresses the growth of MnWO$_4$ in the MNC-4 sample. The XRD result suggests that the CdS nanoparticles were probably decorated on the surface of MnWO$_4$ and were not incorporated into the lattice of MnWO$_4$.

3.2 Surface and morphological studies

Transmission electron microscope (TEM) and high-resolution transmission electron microscope (HR-TEM) analyses were performed to further investigate the morphology and heterojunction formation of the as-prepared samples. Fig. 2 shows the comparative TEM and HRTEM images of the MnWO$_4$ and CdS@MnWO$_4$ samples. Fig. 2a shows the TEM image of pure MnWO$_4$, in which nanoparticles are gathered with a large number of particles forming nanorods. The length of nanorods in the range of approximately 100–150 nm and diameter around 30–35 nm. The HRTEM image (Fig. 2b) shows lattice fringes of the material with an interplanar distance with a calculated $d$ spacing (0.4813 nm) matching well with the $d$ spacing of the (1 0 0) plane of the MnWO$_4$ monoclinic cell. A selected area diffraction (SAED) pattern (inset to Fig. 2a) shows bright spots in the line pattern, confirming that the MnWO$_4$ nanorods are single crystalline in nature. Fig. 2c and d shows the TEM and HRTEM images of CdS@MnWO$_4$, respectively. As can be seen from Fig. 2c and d by comparison with pure MnWO$_4$, the CdS-loaded samples show almost the same nanorods as MnWO$_4$ with the addition of spherical nanoparticles. The spherical nanoparticles of CdS with a size of 10–15 nm were uniformly anchored on the surface of MnWO$_4$ nanorods, which demonstrates the successful formation of a CdS@MnWO$_4$ heterojunction. Furthermore, the HR-TEM images (Fig. 2d) of CdS@MnWO$_4$ also show two distinct sets of lattice fringes with different orientations. The parallel lattice fringes with interplanar spacings of 0.362 nm and 0.360 nm correspond to the (1 1 0) and (100) crystallographic planes of monoclinic MnWO$_4$ and hexagonal CdS, respectively. The inset to Fig. 2c represents

Fig. 1 X-ray diffraction patterns of MnWO$_4$ (MNW-0) and CdS@MnWO$_4$ (MNC-1–4).

Fig. 2 FE-TEM images of pure MnWO$_4$ (a, b) and (c, d) CdS@MnWO$_4$ nanorods (MNC-3). The inset shows the corresponding SAED pattern.
the SAED image of the sample, which confirms the single-crystalline nature of MnWO₄.

To study the growth kinetics of morphology (more specifically the nucleation process, crystal growth, and Ostwald’s ripening process), we employed water as a reaction medium at 180 °C temperature. After the evaluation of the morphological features of as-synthesized CdS@MnWO₄ nanoheterostructures, we have proposed a growth mechanism for the formation of nanoheterostructures. It is well known that two main parameters affect the growth of a crystal: i.e. temperature and the supersaturation of the solution. A highly supersaturated solution was obtained to study during the crystallization where amorphous fine particles act as precursors under hydrothermal conditions at 180 °C. This growth process is called the Ostwald ripening process. At the beginning of the reaction, nucleation takes place in a supersaturated solution; then there is the formation of small nanoparticles. These nanoparticles self-align and form nanorods. In a solvothermal reaction, MnWO₄ nanorods with a length of 150 nm and width of 50 nm are formed at the expense of the self-alignment of MnWO₄ nanoparticles with prolonged reaction time (Scheme 1). The TEM images also suggest that nanorods grow in the direction of the (1 1 0) plane at the expense of smaller nanoparticles, as discussed above. When the growth of MnWO₄ nanoparticles is allowed in the presence of cadmium nitrate and thiourea, the CdS nanoparticles are grown on the surfaces of the MnWO₄ nanorods. Cadmium nitrate (Cd(NO₃)₂·6H₂O) and thiourea (CH₄N₂S) react under the hydrothermal conditions and form Mn(NO₃)₂ + Na₂WO₄ → MnWO₄ + 2NaNO₃ (1)

Cd(NO₃)₂ + NH₂CSNH₂ + 2H₂O → CdS + CO₂ + 2NH₄NO₃ (2)

Overall reaction:

Mn(NO₃)₂ + Cd(NO₃)₂ + Na₂WO₄ + NH₂CSNH₂ + 2H₂O → MnWO₄ + CdS + 2NaNO₃ + CO₂ + 2NH₄NO₃ (3)

Initially, MnWO₄ formation takes place and after the saturation of MnWO₄, CdS formation takes place on the surface of the MnWO₄ nanorods via reaction (2).

Scheme 1 shows the formation of MnWO₄ nanorods and the anchoring of CdS nanoparticles on the surface of MnWO₄. Under hydrothermal conditions, the Mn²⁺ and WO₄²⁻ ions react with each other and form MnWO₄ nanoparticles. Furthermore, due to prolonged hydrothermal treatment, the nanoparticles self-align in one direction and form nanorods as per the crystal growth phenomenon (Ostwald ripening) as discussed above (Scheme 1a). Furthermore, MnWO₄ nanorods become saturated with Cd²⁺ and S²⁻ ions (Scheme 1b) and form CdS nanoparticles on the surface under hydrothermal conditions.

3.3 Optical properties

The optical properties of the as-synthesized material were examined by UV-visible diffused absorption spectra. Fig. 3 shows the comparative UV DRS spectra for pure MnWO₄ nanorods (MNW-0) and different concentrations of CdS@MnWO₄ (MNC-1, 2, 3, and 4) nanoheterostructures. Fig. 3 reveals that the absorption edges of pure MnWO₄ (MNW) show two edges at approximately 455 nm and 575 nm, respectively. In the case of MnWO₄, weak absorption at 575 nm is due to the d² electronic configuration of Mn(II) causing a d–d electronic transition which is spin forbidden; therefore it shows a weak absorption peak at 575 nm. In comparison to pure MnWO₄, the absorption edges of the CdS@MnWO₄ samples were gradually red-shifted with increasing CdS content. The following formula can be used to calculate the band gap energy for one semiconductor: 

\[ \text{hv} = A(h\nu - E_g)^{1/2} \]

where \( h \nu \), \( A \), and \( E_g \) are the light energy, absorption energy, constant value, and the band gap of the semiconductor and \( n \) is the transition type of the semiconductor: \( n = 1 \) for a direct transition and \( n = 4 \) for an indirect transition. The calculated band gaps for MnWO₄ and CdS were 2.74 and 2.34 eV. With an increase in CdS the band gap of CdS@MnWO₄ is closer to that of CdS (ESI I Table 1†).
This indicates that coupling with CdS could narrow the band gap value of MnWO₄, thus leading to improved optical absorption in the visible light region (Table 1).

Photoluminescence spectra (PL) were performed to study different energy states available between the VB and the CB which are responsible for radiative recombination. Fig. 4 shows comparative room-temperature PL spectra of as-synthesized pure and CdS@MnWO₄ excited at a wavelength of 325 nm. Pure MnWO₄ shows a broad emission peak in the wavelength range 525–530 nm, well matching previous reports. The PL emission spectra for pure MnWO₄ show bands at wavelengths of 416, 452, 470, 497, 482, and 576 nm, attributed to the transition from the 1A¹ ground state to the high vibration level of 1T₂ and from the low vibration level of 1T₂ to the 1A¹ ground state within tetragonal WO₄²⁻ groups. The PL spectra for MNC-1, 2, 3 and 4 show two strong emission peaks centered at wavelengths of 468, and 530–540 nm that can be assigned to CdS and MnWO₄, and peaks contributing to the band-to-band PL phenomenon with the energy of light equal to the band gap energy. The peak observed at wavelength 530–540 nm is assigned to the trapped electron–hole pairs or excitations bound to ionized donors and shows an intrinsic character with surface defects due to CdS.

From the PL spectra it is clear that with an increase in the concentration of CdS on MnWO₄ a redshift in the peak at 530 nm is observed, due to an increase in the concentration of CdS nanoparticles. From Fig. 4 it can also be observed that with an increase in CdS loading on MnWO₄ nanorods, the PL intensity decreases, suggesting a lower electron–hole pair recombination rate due to the presence of surface defects. The above results show that surface modification by CdS on MnWO₄ drastically decreased the PL intensity.

Samples MNW-0 and MNW-3 were employed for Raman analysis and the corresponding data is shown in Fig. 5. All the peaks were observed in the range 500–1200 cm⁻¹ at room temperature. Pure MnWO₄ shows a strong intense band observed at 885.3 cm⁻¹ corresponding to Ag modes originating from the symmetric stretching vibration of a short terminal W–O bond, while the asymmetric stretching vibration from the W–O bond is located at 774 cm⁻¹ corresponding to B₉ modes. Some weak bands contribute to asymmetric stretching vibration modes of longer W–O bonds, at 696, 516, 548 cm⁻¹, deformation vibration of short W–O bond in (W₂O₇)ₙ chains, and 330 and 397 cm⁻¹ vibration modes of Mn–O bonds. The sample MNC shows broad peaks at 297, 592, and 882 cm⁻¹ associated with CdS. All three peaks are assigned to the first overtone mode (LO), second overtone mode (2LO) and third overtone mode (3LO) of CdS, respectively. Samples MNC-1–4 show the presence of both CdS and MnWO₄, providing clear evidence for the formation of a CdS@MnWO₄ heterojunction.

### Table 1

| Sr. no. | Sample        | H₂ evolution rate (µmol h⁻¹ g⁻¹) |
|---------|---------------|---------------------------------|
| 1       | MNW-0         | 153                             |
| 2       | MNC-1         | 916                             |
| 3       | MNC-2         | 1368                            |
| 4       | MNC-3         | 3218                            |
| 5       | MNC-4         | 2479                            |
| 6       | Pure CdS      | 380                             |

3.4 Photocatalytic study

3.4.1 Photocatalytic H₂ evolution from H₂O splitting: Photocatalytic H₂ generation was studied with a water-splitting
reaction using Na₂S/Na₂S₂O₃ solution under solar light irradiation in which Na₂S/Na₂S₂O₃ acts as a sacrificial agent. Hydrogen measurement was performed under solar light at room temperature and the amount of hydrogen was determined by gas chromatography (GC). No hydrogen gas was detected in the absence of a photocatalyst or in the dark, indicating that hydrogen is due to the presence of light with a semiconductor photocatalyst. For the hydrogen generation experiment, we used 70 mL of DI water, and a mixture of 0.25 M Na₂S and 0.35 M Na₂S₂O₃ was used as a sacrificial agent. The role of a sacrificial agent is not only to resist photocorrosion but to oxidize S₂²⁻ into S²⁻, which supports the enhancement of free electrons. Previous reports show the detailed mechanism of the water splitting reaction in which the semiconductor absorbs solar light equal to or greater than the band gap energy, generating electrons in the CB and holes in the VB. The redox reaction takes place on the surface of the semiconductors with adsorbed species. The photogenerated holes from the VB irreversibly oxidize S₂²⁻, which is reduced back to S²⁻ by Na₂S₂O₃ and is instantaneously adsorbed on the semiconductor surface, producing protons (H⁺) and free radicals, while electrons from the CB reduce H⁺ ions into molecular hydrogen H₂. Fig. 6 shows the time-dependent H₂ evolution rates of all as-synthesized materials, indicating that MnWO₄ NRSs and CdS alone produced relatively very low amounts of hydrogen, 3.53 μmol h⁻¹ and 380 μmol h⁻¹ g⁻¹ (ESI II†), but CdS@MnWO₄ exhibits 3218 μmol h⁻¹ g⁻¹, which is 21 times higher than MnWO₄. Scheme 2 shows that after the decoration of CdS nanoparticles on MnWO₄, there is enhanced photocatalytic activity. The rate of hydrogen production increases with the amount of CdS content. The maximum hydrogen production of 3218 μmol h⁻¹ g⁻¹ was obtained for sample MNC-3 CdS decorated MnWO₄. Furthermore, it is observed that with an increase in CdS to 20% (MNC-4) CdS@MnWO₄, the rate of hydrogen production decreases to 2479 μmol h⁻¹ g⁻¹. The decrease in photocatalytic activity for MNC compared with MNC-3 is due to rapid electron–hole pair recombination and a shielding effect towards light absorption due to excess CdS decoration. Furthermore, the PL study also supports the finding that the lower the PL intensity, the higher the separation rate of photoinduced charges, and, possibly, the higher the photocatalytic activity. Sample MNC-3 shows lower PL intensity compared to MNC-4, a higher separation rate of photoinduced charges, and, possibly, higher photocatalytic activity. Historically, CdS-decorated nanomaterial heterostructures exhibited enhanced photocatalytic activity towards hydrogen generation and effective charge carrier separation. For example Chava et al. reported 1D–0D CdS–SnS₂ nanorods for excellent photocatalytic hydrogen evolution activity. Similarly, Shandong et al. prepared a CdS/NiS hybrid photocatalyst where NiS acts as a cocatalyst which exhibits maximum hydrogen evolution (with 793.6 μmol h⁻¹). The enhanced photocatalytic activity was due to intimate contact between CdS/NiS reducing the electron–hole pair recombination rate. In that direction recently, we have reported CdS-decorated CdWO₄ nanorods for hydrogen generation and efficient dye degradation. The above results show that CdS-based semiconductor heterostructures effectively enhance stability and photocatalytic activity. Similarly, in the present work with CdS nanoparticles decorated on MnWO₄ nanorods, the advantage of CdS is its ability to harvest solar light. In addition, the heterojunction between CdS@MnWO₄ inhibits the electron–hole pair recombination rate, thereby enhancing photocatalytic activity. Furthermore, the MnWO₄ nanorods provide space to protect CdS from the photocorrosion problem. Hence, the optimum quantity of CdS on MnWO₄ enhances photocatalytic hydrogen generation under solar light. Furthermore, a recycling study shows stable hydrogen evolution under solar light (ESI: III Table 2†).

$$\text{Semiconductor} \rightarrow e^- + h^+ \quad (4)$$

**Oxidation:**

$$\text{SO}_4^{2-} + 2\text{OH}^- + 2h^+ \rightarrow \text{SO}_4^{2-} + 2\text{H}^+ \quad (5)$$

$$2\text{S}^{2-} + 2h^+ \rightarrow \text{S}_2^{2-} \quad (6)$$

$$\text{S}_2^{2-} + \text{SO}_4^{2-} \rightarrow \text{S}_2\text{O}_3^{2-} + \text{S}^{2-} \quad (7)$$

$$\text{SO}_4^{2-} + \text{S}^{2-} + 2h^+ \rightarrow \text{S}_2\text{O}_3^{2-} \quad (8)$$

**Reduction:**

$$\text{H}^+ + 2e^- \rightarrow \text{H}_2 \quad (9)$$

### 3.4.2 Possible mechanism of photocatalytic activity using CdS@MnWO₄

The Z-scheme photocatalytic mechanism of the CdS@MnWO₄ nanoheterostructure is proposed and discussed. It has been well reported that the photocatalytic activity of a semiconductor depends on the optical band gap, crystal structure, electron–hole pair recombination rate, etc. However, photocatalytic activity depends specifically on band structure:

![Fig. 6 Photocatalytic hydrogen generation via H₂O splitting with CdS@MnWO₄: (a) MNW-0 (black), (b) MNC-1 (red), (c) MNC-2 (orange), (d) MNC-3 (purple) and (e) MNC-4 (blue).](image-url)
i.e. the position of the bottom of the VB and the top of the CB of both MnWO₄ and CdS. The valence band and conduction band potentials of MnWO₄ and CdS can be calculated using the following equations:

\[
E_{\text{VB}} = \chi - E_{\text{fb}} + \frac{1}{2}E_g
\]

\[
E_{\text{CB}} = \chi - E_{\text{fc}} - \frac{1}{2}E_g
\]

where \(E_{\text{VB}}\) and \(E_{\text{CB}}\) are the valence band and conduction band edge potentials, respectively, \(\chi\) is the electronegativity of the semiconductor, which is the geometric mean of the electronegativity of the constituent atoms. \(E_{\text{fb}}\) is the energy of free electrons on the hydrogen scale (about \(-4.5\) eV) and \(E_{\text{fc}}\) is the band gap energy of the semiconductor. As per the literature, the values of \(\chi\) for MnWO₄ and CdS have been calculated as \(6.12\) eV and \(5.04\) eV, respectively.\(^{24}\) Based on band gap positions, the band edge potentials of the VB and CB for MnWO₄ are \(2.95\) and \(0.27\) eV while for CdS they are \(2.18\) and \(-0.12\) eV, respectively.\(^{23}\)

Based on the above values, a possible mechanism is illustrated in Scheme 2. In the presence of solar light, CdS and MnWO₄ with their band gaps of \(2.3\) and \(2.68\) eV, respectively, undergo photoexcitation.\(^{23}\) However, pure MnWO₄ shows poor photocatalytic activity due to its wide band gap compared with CdS. In the present case, a CdS@MnWO₄ photocatalytic mechanism is proposed via a Z-scheme, as shown in Scheme 2. As illustrated in Scheme 2 under visible light both CdS and MnWO₄ are excited and generate photoinduced electron–hole pairs. The electrons from CdS transfer to MnWO₄ via strong intimate contact through the interface due to the more negative Fermi level of CdS, leaving holes on the CdS. Due to the transfer of electrons from the CB of CdS which have the energy to stride over the potential barrier, they can be transported from CdS to MnWO₄. Therefore, the existence of a potential barrier goes against the transmission of photoinduced electrons from the CB of CdS to the CB of MnWO₄. The same principle can be applied to the transfer of photoinduced holes from the VB of MnWO₄ to the CB of CdS. In construction, the band structure is more suitable to transfer photogenerated electrons from the CB of MnWO₄ to the VB of CdS: i.e. electrons migrate from the CB of CdS to the VB of MnWO₄ through the Z direction.\(^{46}\) This migration process leaves the photoexcited electrons in the CB of CdS and photoexcited holes in the VB of MnWO₄. The electrons from the CB of CdS possess a strong reducibility ability which can drive hydrogen generation. This enhancement occurs due to the Z-scheme heterostructure, which facilitates an effective electron–hole pair separation and also enhances the redox ability of a photocatalyst.\(^{47}\) Hence, the Z-scheme mechanism enhances the recombination of the electron–hole pair in the case of CdS@MnWO₄.

### 4. Conclusions

In summary, hierarchical CdS nanoparticles have been decorated on the surface of MnWO₄ architectures that have been constructed via an \textit{in situ} hydrothermal method. The structural, optical, and morphological properties of as-prepared CdS@MnWO₄ with varied amounts of CdS were studied systematically. FE-TEM analysis showed the existence of a heterojunction between CdS and MnWO₄ nanorods, and the effect of CdS decoration on MnWO₄ was investigated by a photoluminescence study. In the case of CdS@MnWO₄, CdS acts as a sensitizer for MnWO₄ to capture sunlight and also acts as a co-catalyst to promote the electron–hole pair separation rate under solar light irradiation. The heterojunction between CdS@MnWO₄ exhibits excellent photocatalytic \(\text{H}_2\) evolution \textit{via} \(\text{H}_2\text{O}\) splitting under natural sunlight. The encouraging results presented in this work demonstrate the potential of CdS@MnWO₄ as an active photocatalyst for hydrogen evolution from water.

### Conflicts of interest

There are no conflicts to declare.

### Acknowledgements

BBK & YAS would like to thank the Ministry of Electronics and Information Technology (MeitY), the Government of India for financial support, and C-MET Pune for providing research facilities. AKK would like to thank ASPIRE SPPU for financial support under the project scheme. SWG would like to thank SPPU, Physics Department for technical support. The authors would like to thank the Nanocrystalline materials group for kind support.

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