Efficiency and stability aspects of CdS photoanode for solar hydrogen generation technology

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Abstract. Photoelectrochemical (PEC) cell based technology is expected to be one of the easiest green technologies to harness and to convert available solar energy into hydrogen [1]. Among the known systems of GaAs, Si, GaP and CdS- Cadmium sulphide is one of the best suited PEC materials that display a balance between its efficiency and stability. It has capability to absorb the visible light photons (E~1.5eV – 3eV), and displays the band-energetics that suits for water-splitting reaction (H₂O→H₂+O₂), that ultimately is based on the electronic and optical structure of the sulphides. However, the photo-induced dissolution of CdS in an electrolyte during its photo-illumination in PEC cell is its major drawback [2]. Though arsenides and phosphides show higher efficiency however CdS exhibits significant stability. In contrast though TiO₂/ ZnO show good stability but CdS displays good optical response towards visible light photons as compared null response of titanate like systems. This necessitates one to identify the practical way to inhibit the photocorrosion in case of CdS photoanodes which is mainly facilitated due to interaction of photogenerated holes with CdS lattice. In past, Pt/ RuO₂/ Ru modified CdS surface were found to control the unwanted photocorrosion [3]. Commercially, usage of such materials is un-economic option for any technological usage. The present work discusses that with advent of present day new synthetic routes how the dynamics of photo generated holes and electrons can be controlled to improve the stability and efficiency of the sulphide photoanodes, which in turn shows an improvement in the performance and stability of the PEC cell for desirable technological applications.

1. Introduction

A renewable hydrogen generation by photoelectrochemical water-splitting reaction is highly desirable for ever-growing energy demands. Photoelectrochemical (PEC) hydrogen production through splitting of water under sunlight is one of the most promising technologies for a future hydrogen economy [1, 4]. The cadmium chalcogenides comprise one of the most important class of materials in the photoelectrochemical research. CdS exhibits a direct band gap of ~2.42eV, and is considered to be an excellent visible light responsive material [5]. Interestingly, it possesses suitable band-edge positions desirable for cleavage of water molecule into hydrogen and oxygen. Despite these advantages,
chalcogenides are associated with a problem of photocorrosion that hampers their long term stability in the PEC application. In past, there have been different strategies, adopted to curb the photocorrosion viz. (1) Use of the sacrificial agent in an electrolyte which acts as a scavenging agent and consumes the holes participating in the photocorrosion reaction [3,6]; (2) Loading some inert metal on the semiconductor surface so that it behaves as a catalyst to increase the rate of oxygen or hydrogen evolution [7]; (3) Modification of the semiconductor surface with metal oxide/ polymers to protect the semiconductor from electrolyte [8]. This is schematically illustrated in figure 1. Among all the strategies the most attractive is the protection of the semiconductor surface by metal-oxide thin layer that resist the electrolyte, and at the same time allows the sunlight to be absorbed by the electrode.

With the advent of nanostructuring technologies, one is able to tailor the electrode surface using nano-dimensional adsorbates. This is expected to render a favourable and constructive physical mechanism such as quantum size effects, quantum tunnelling, etc, for the modified configuration of the electrode. Ultimately, we expect these modified structures lead to a dramatically improved optoelectronic performance of the photoelectrodes. In order to demonstrate the expected “nanostructure induced performance” of CdS electrode, we selected two model metal oxides (MO; M = Ti, Nb) viz., TiO$_2$ and Nb$_2$O$_5$. TiO$_2$ and Nb$_2$O$_5$ are considered as the most stable metal oxides under wide pH range. TiO$_2$ has been regarded as the most promising system for passivation of chemically unstable semiconductors (GaAs, Si, GaP and CdS) due to its high photochemical stability, non-toxicity and low cost. Similarly, Nb$_2$O$_5$ (+V oxidation state) shows higher stability in the pH range 0.1-12.2 rather than NbO$_2$ (+II oxidation state) [9]. In present work, we have used these metal oxides as “nanoparticle model” systems to modify the CdS photoanode to improve its stability. We have attached metal oxide nanoparticles using Thioglycerol (TG) as an organic linker by making use of a simple adsorption technique, over the photoanode surface. These electrodes were investigated in depth to understand the underlying physics and the electrochemical aspects those are responsible to attain stable photoanode for PEC cell.

**Figure 1.** Schematic displaying different strategies to inhibit the photocorrosion process in photocatalysts
2. Experimental Section

2.1. Materials
CdCl₂ (Sigma-Aldrich, 99.999%), (NH₄)₂CS (Sigma-Aldrich, 99.9%), NH₄[NbO (C₂O₄)₆(H₂O)₂]ₙH₂O (CBMM, Brazil), TiCl₄ (Sigma-Aldrich, ≥ 99.0%), H₂O₂ (Sigma-Aldrich, 30% w/w), Thioglycerol (Sigma-Aldrich, ≥ 97%), Fluorine doped Tin oxide, FTO (Pilkington, TCO-15) glass substrate (12-15Ω/sq.) and Deionized water (18.2 MΩ.cm) were used.

2.2. Deposition of CdS thin film and fabrication of photoelectrode
The CdS thin films were deposited onto preheated FTO substrate by computer automated spray pyrolysis deposition technique. Its schematic is shown in figure 2. Nanostructured CdS thin films were deposited by optimization of various parameters like flow rate, number of deposition cycles, duration of the deposition, temperature and area of deposition as reported in our earlier work [10]. The precursor solution containing mixture of CdCl₂ (0.1M) and (NH₄)₂CS (0.1M) were used for the deposition onto FTO substrate at 350°C with flow rate of 5ml/min. The nozzle to substrate distance of ~23cm was maintained throughout the experiment.

The CdS electrodes were fabricated from the films by exposing active area of unit dimension over the film. The electrical contact was made over the undeposited area of FTO substrate, for applying desired biasing voltage. The undesired film area was electrically insulated using an epoxy. Thus obtained photoelectrode was used for the surface modification and further for the PEC hydrogen generation.

2.3. Preparation of TiO₂ and Nb₂O₅ oxide nanoparticles
In order to synthesize nanoparticles of metal oxides, hydrolysis and hydrothermal techniques were used for TiO₂ and Nb₂O₅ respectively. TiO₂ nanoparticles were synthesized via known procedure in the literature [11]. A precise concentration of titanium tetrachloride (TiCl₄) is dissolved in the deionized water at ice-cold temperature and is mixed with an ammonia solution. The resulting mixture was kept under stirring condition for an hour and refluxed for ~18h. The precipitate from the refluxed mixture was collected by centrifugation and washed with deionized water for the removal of un-

![Figure 2](image-url)
reacted impurities. Thus obtained precipitate was air-dried to obtain the free standing powder of nanoparticles. This yielded 2.5nm sized TiO$_2$ nanoparticles. Further, Nb$_2$O$_5$ nanoparticles were synthesized by hydrothermal method [12]. In brief, 8g of ammonium niobium oxalate powder was dissolved in deionized water (100 mL) to obtain a transparent solution. To this, H$_2$O$_2$ (30% by vol.) was added that led to the formation of niobium peroxo complex, a transparent yellow solution. The obtained solution mixture was then transferred to a teflon lined autoclave (200 mL) and subjected to 120°C for 9hrs. After the reaction, finally obtained white precipitate was washed thoroughly with water-ethanol mixture and separated by centrifugation. This yielded Nb$_2$O$_5$ nanoparticles of 5nm size. These MO nanoparticles were used for the photoanode surface modification.

2.4. Surface modification of CdS photoanode by metal oxide nanoparticles
The surface of CdS photoanode was modified by MO nanoparticles by adsorption mechanism via linking agent. This was reported to yield a stable and efficient photoanode during the PEC measurements [13]. Figure 3 schematically illustrates the procedure used for surface modification. TG was used as linking agent for the surface modification with 0.1 v/v % concentration, after optimization that yielded best nanoparticles adsorption and thus an improved PEC performance. An organic linker helps in yielding uniform surface adsorption of nanoparticles over the CdS surface. The CdS surface linked by TG was further treated by nanoparticles by immersing the photoanode in nanoparticle dispersion. Thus nanoparticle dispersion in aqueous medium was ultrasonicated for 20 min prior to electrode immersion. An immersion time of 7 min was used for this purpose. Thus obtained electrode was dried and used for the further measurements.

2.5. Physico-Chemical characterization of the photoanode
The crystal structure of the nanostructured films were investigated using X-ray diffraction analysis. For this, Bruker AX D8 XRD diffractometer equipped with Cu K$_\alpha$ ($\lambda = 1.514\text{Å}$) X-ray gun was used. The scan was performed in the range of 2$\theta = 10$-70$\degree$ with an increment of 0.01$\degree$/s at the grazing angle of incidence 0.2$\degree$. A detailed elemental and compositional analysis of the bare and surface modified CdS films was done by X-ray photoelectron spectroscopy (Omicron model). The UV-Vis absorption analysis was done by using Perkin Elmer Lambda 650 spectrometer. The PEC analysis was carried out using an electrochemical workstation (PARSTAT model 2273) to obtain photocurrent density of the photoanode of unit area. A PEC reactor cell with three electrode configuration consisting of photoanode as working electrode (WE), standard calomel electrode (SCE) as reference electrode (RE) and graphite as counter electrode (CE) was used. An aqueous mixture of Na$_2$S (0.1M) and Na$_2$SO$_3$ (0.1M) was used as an electrolyte to maintain inherent electrode stability against photocorrosion of the CdS film. In order to study the PEC performance and solar hydrogen production, solar simulator
Oriel Model 91160) equipped with A.M.0, A.M.1.0 and an AM1.5 Global (Newport) filter was utilized. The irradiance of 80mW/cm$^2$ was used in the present case. The incident photon current conversion efficiency (IPCE) measurements were carried out using an Oriel monochromator capable of generating desired wavelengths (accurate up to ±2nm) in the range of 200-900 nm. Quantitative estimation of evolved hydrogen was done by using gas chromatograph-GC (Schimadzu 2010 AFT) equipped with thermal conductivity detector was used for hydrogen detection and analysis.

3. Results
The bare and modified CdS photoanode has been used throughout, to the study structural, elemental, optical and charge transfer properties.

3.1. Structural and elemental characterization of bare and modified CdS photoanodes
Figure 4 shows X-ray diffraction spectra of bare and the modified CdS photoelectrodes. The CdS films exhibited hexagonal phase of CdS that belongs to P63MC (JCPDS file No. 00-006-0314) space group. The background showed weak low intensity peaks of SnO$_2$ (FTO) due to the substrate. The existence of TiO$_2$ and Nb$_2$O$_5$ nanoparticles over the surface is not detected as it is beyond the detection limit of XRD. This confirms that the modification does not alter the XRD pattern of CdS. It is important to mention that the particle size of metal oxide nanoparticles was estimated separately from XRD and TEM (Transmission Electron Microscopy) of nanoparticle powders. Nanoparticle characterization is not included here, but the details can be found elsewhere [12-13]. Briefly, the nanoparticle sizes were calculated using Debye-Scherer’s formula [14] and were found to be 2.5 and 5 nm for TiO$_2$ and Nb$_2$O$_5$ respectively.

\[ D = \frac{0.9\lambda}{\beta \cos \theta} \]  

where, $D$-particle size (nm), $\lambda$-wavelength (nm), $\theta$-diffraction angle, $\beta$-FWHM.

![Figure 4. XRD patterns of bare CdS and MO nanoparticles modified CdS films.](image-url)
Figure 5 shows XPS analysis of bare and modified CdS photoelectrode before PEC measurements in the form of survey scan. It indicates the presence of Cd 3d and S 2p lines at B.E. ~160.9eV and 404.69eV respectively along with carbon peak. This clearly shows that the film consists of a stoichiometric composition of CdS. For modified CdS film with TiO$_2$ nanoparticles, the presence of Ti 2p at 457.17eV and O 1s at 529.56eV is confirmed. Further, the spectrum of Nb$_2$O$_5$ modified CdS displays the peaks due to Nb 3d and O 1s. An in depth analysis of region wise scan of Ti/Nb/Cd/S/O by deconvolution [15], confirms that MO nanoparticles are linked to the CdS via TG linking agent.

3.2. Optical characterization of bare and modified CdS photoanodes

The UV-Vis absorption spectra of bare and modified CdS photoanode are shown in the figure 6. It can be clearly seen from the UV spectrum that as compared to bare CdS spectrum, the modified one shows blue shift in the absorption due to the existence of nano-sized particles of larger band gap (~3.2eV). The study reveals that the optical property of the CdS film remains unaffected after the adsorption of TG and the presence of these particles screens the overall surface which leads to a decrease in the absorption of the CdS film in visible range.

Figure 6. UV-Vis absorbance spectra of bare CdS film, TG, TiO$_2$, Nb$_2$O$_5$ nanoparticles modified CdS films.
3.3. Photoelectrochemical measurements of modified CdS photoanodes

The surface modification of CdS with nanoparticles is done to improve the efficiency of photoanode. The photocurrent density, charge transfer mechanism, efficiency and hydrogen rate were analysed with PEC measurement. This yields the performance of respective photoanodes. Figure 7 shows the comparative chronoamperometric curves for the modified CdS w.r.t. bare CdS photoanode at 0.2V. The photocurrent density of bare CdS electrode was found to be 480µA/cm² while that of TiO₂ and Nb₂O₅ modified CdS was 1.2mA/cm² and 1mA/cm². The reduced photocurrent of CdS is due to the fast recombination of photogenerated electron-hole pairs that largely depends on the density of surface states in the semiconductor that acts as an electron trapping center. But, the MO nanoparticle modified CdS has enhanced photocurrent. It is attributed to the formation of passivating layer on the surface which in turn reduces the recombination rate of the photogenerated charge carriers.

3.3.1. Incident photon to current conversion efficiency

It is one of the most important characterizations which provides information about how efficiently a cell converts photons of a particular frequency into electrons and is known as wavelength dependent efficiency. An incident light from monochromator falling on the photoanode generates an output current that can be used to calculate the number of electrons generated. IPCE is given by the relation [16]

\[
IPCE = \frac{1240 \times I}{\lambda \times P} \times 100\%
\]

Where I – photocurrent density (A/cm²), P - source power (W/cm²) and \( \lambda \)- wavelength (nm). Figure 8 shows that the calculated IPCE for MO nanoparticles modified CdS photoanode was found to be 22% at 470nm and 18% at 480nm respectively. These values are found to be enhanced as compared to bare CdS photoanode (8%). This high efficiency improvement in turn generates hydrogen from water during the hydrogen evolution reaction.
3.4. **Photoelectrochemical stability studies of modified CdS photoanodes**

Apart from the PEC activity and stability, long-term PEC performance potrays main concerns for the development of efficient photocatalystic electrode. Specifically, this needs the study of related parameters, such as degradation of electrode-corrosion that changes the electrode surface composition as well as releases mineral impurities in the electrolyte solution. Hence to detect the deterioration of photocatalyst due to photocorrosion, a long hour chronoamperometric measurement is desirable. Figure 9 shows the stability measurements for bare and modified CdS carried out for 9hrs at 0.2 biasing voltage in photocurrent Vs time plot. It can be observed that the photocurrent of bare CdS decreases abruptly with the time, whereas the modified CdS photoanode shows a constant photocurrent during 9hrs of measurement indicating a drastic improvement and a sustained photocurrent over the time of measurement.

![Figure 8. IPCE curve of bare and MO modified CdS photoanode.](image)

![Figure 9. Chronoamperometric curve recorded for 9hrs of stability for bare and modified CdS photoanodes.](image)
4. Discussions
Earlier section has clearly demonstrated that the nanoparticles induced photocurrent enhancement and stability is due to the modification of CdS photoanode. It is important to understand the underlying mechanism that has led to such drastic improvement in the efficiency and stability. Accordingly, we have analyzed and explained this effect in terms of, (1) adsorption of nanoparticles on CdS surface; (2) charge transfer mechanism occurring at electrode/substrate and electrode/electrolyte interfaces.

4.1. Mechanism of surface adsorption process
The surface modification of the CdS photoanode was carried out using chemisorption process, which involves the use TG as organic linkers. As shown in figure 10, this linking agent chemically links two compounds with preferred functional groups. Hence the formation of hybrid structure is due to affinity of CdS and TiO$_2$ and Nb$_2$O$_5$ nanoparticles towards thiol(R-SH) and hydroxyl (-OH) groups.

4.2. Charge transfer mechanism in the modified CdS photoanode
Nanoparticle adsorption over the substrate reduces the charge trapping states over the surfaces of CdS which in turn leads to the changes in the electrode/electrolyte interface. Thus, there is a difference in band energies of the modified CdS w.r.t. bare CdS photoanode. Basically, the charge transfer mechanism in the CdS photoanode involves the following process [17].

- The incident light is absorbed by the CdS photoanode
- When incident light energy is greater than band gap (Eg) of photocatalyst, it absorbs and further excites the electrons from valence band (VB) to conduction band (CB) leaving holes in VB.
- Thus, the photogenerated electrons and holes migrate over the surface of CdS, while some charge carriers recombine to release photons.
- Since the valence band edge of metal (Ti and Nb) oxide is more positive than CdS, hole transfer from CdS to electrolyte can take place only through the “quantum tunnelling” process.
- The electrons at counter electrode produce hydrogen gas whereas holes at working electrode combines with water molecule to produce oxygen gas.
- Due to adsorbed nanoparticles, the surface states on the CdS gets passivated and hence with enhanced photocurrent could be achieved due to the reduced recombination of the photogenerated charge carriers.

4.3. Stability factor
Stability is the most important factor that dictates the life of a photoanode, which in turn yields to an efficient PEC cell. We have defined the stability factor to quantify the photoelectrode performance. It has been defined in depth in our past report [12]. Briefly, it depends on several, physical, chemical and

![Figure 10. Schematic of adsorption mechanism of MO nanoparticles on CdS surface using TG as linking agent.](image-url)
other factors. We have defined this new parameter ($\sum_{\text{photoelectrode}}$) which is function of several dependent parameters (physical/chemical/others) as described below:

$$\Phi_{\text{photoelectrode}} = \Phi (\text{physical}) \cdot \Phi (\text{chemical}) \cdot \Phi (\text{others})$$  \hspace{1cm} (3)

Where, 

$\Phi$ (physical) – physical properties of electrodes correlated to stability viz. crystal structure, orientation, thickness, area, geometry.

$\Phi$ (chemical) – pH of electrolyte, electrolyte composition, concentration of electrolyte.

$\Phi$ (others) – temperature, time, stirring and photocurrent density.

It is imperative that the stability ($\sum_{\text{photoelectrode}}$) is multiple-parameter dependent function involving various processes, and thus it is difficult to describe it quantitatively. However, in order to simplify its quantitative estimation in present study, we have considered the variation of photocurrent with time as a means to estimate the time-dependent stability of a photoanode; accordingly, we propose “photoanode-stability” to be a simple function of photocurrent density and illumination time, assuming other parameters constant. This has led to a stability factor as:

$$\sum_{\text{photoelectrode}} \% = \frac{\Delta_{\text{CdS}} - \Delta_{\text{modified}}}{\Delta_{\text{CdS}}} \cdot 100\%$$

$$\Delta_{\text{modified}} \rightarrow \Delta_{\text{CdS}}, \sum_{\text{photoelectrode}} \rightarrow 0$$

$$\Delta_{\text{modified}} \rightarrow 0, \sum_{\text{photoelectrode}} \rightarrow 1$$

Where $\Delta_{\text{photoelectrode}}$ is slope of “I vs. t” curve of the photoelectrode, given by:

$$\Delta = \frac{\partial I}{\partial t} = \frac{I(t_2) - I(t_1)}{t_2 - t_1}$$  \hspace{1cm} (5)

Here, $I(t_1)$ is the photocurrent at time ‘$t_1$’ and $I(t_2)$ is the photocurrent at time ‘$t_2$’.

Accordingly, the slope of I - t curve for CdS ($\Delta_{\text{CdS}}$) and modified photoanode ($\Delta_{\text{modified}}$) were calculated from figure 9. Subsequently, stability ($\Sigma$) is estimated for each modified photoanode w.r.t. the bare CdS photoanode. Figure 9 clearly reveal that, if the decay in the photocurrent of photoanode is comparatively faster as in case of CdS, it indicates a poor stability. However, if there is no decay in the photocurrent as seen in modified photoanode, then it indicates the photoanode has 100% stability. Photocurrent performance of photoanode dictates the photoefficiency and stability of hydrogen evolution reaction. Accordingly, we studied quantitatively the long-term PEC hydrogen evolution over

| Material  | Band gap, Eg (eV) | Photocurrent density (mA/cm²) | H₂ Rate (µmol/h) | Slope ($\Delta$) | Stability Factor (\(\Sigma\) in %), at illumination time [T] |
|-----------|------------------|-------------------------------|-----------------|-----------------|----------------------------------------------------------|
| CdS       | 2.42             | 0.48                          | 1.7             | 12.7            | 0 [1 day]                                                |
| CdS/Ti    | 2.50             | 1.20                          | 22              | 0.0             | 100 [1 day]                                              |
| CdS/Nb    | 2.52             | 1.00                          | 10              | 5.5             | 99.8 [0.4 day]                                           |
bare and modified electrodes. This study clearly indicated modified CdS performs excellently w.r.t. efficiency and stability in contrast to the poor performance of less stable bare CdS electrode. Table 1 summarizes the variation in the stability i.e. photocurrent density, hydrogen rate, slope of “I vs. t” and stability factor for all electrodes.

5. Conclusion
This addresses the main issue of stability improvement of Cd chalcogenides i.e. mainly CdS by using nanoparticle induced surface modification of the electrode. Chemically synthesized MO nanoparticles (TiO$_2$ and Nb$_2$O$_5$) when linked via TG rendered a stability improvement to the modified CdS electrode. This also led to increased hydrogen evolution of one order as compared to the bare CdS photoanode. This also demonstrated that TiO$_2$ modified CdS films are more stable than Nb$_2$O$_5$ modified CdS films. This study clearly indicates that MO nanoparticle induced surface modification is best & economic way of stabilizing the CdS photoanode for hydrogen production technology.

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