

## An Advanced Hybrid Nanocomposite Film and Its Photocatalytic Water Electrolysis Response

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### ABSTRACT

*Photocatalytic water electrolysis is a key target for the development of sustainable hydrogen economy for our future energy system. The formation of highly ordered titanium dioxide (TiO<sub>2</sub>) nanotubes without bundling is essential for high efficiency in photocatalytic water electrolysis response. Based on the results obtained, highly order TiO<sub>2</sub> nanotubes film was successfully formed through electrochemical anodization method. An anatase phase of TiO<sub>2</sub> nanotubes film was formed under calcination temperature of 400 °C for 4 hours. Then, continuous effort has been carried out to further enhance the photocatalytic water electrolysis response by incorporating an optimum content of cadmium selenide (1 at% CdSe) species on TiO<sub>2</sub> nanotubes using chemical bath deposition technique. It was found that the presence of about 1 at% CdSe species on TiO<sub>2</sub> nanotubes film showed an improvement in hydrogen generation (1.7 times) than that of pure TiO<sub>2</sub> nanotubes film because it acted as an effective mediator to trap the photo-induced electrons and minimizes the recombination of charge carriers.*

**Keywords:** Hydrogen, Photocatalytic, Nanocomposite Film, Electrons Acceptor, Cadmium Selenide

### 1. INTRODUCTION

Today, hydrogen (H<sub>2</sub>) gas has been generally identified as environmentally clean fuel and possibly the best substitute for our current fossil fuel (e.g. coal, oil and natural gas) in order to secure the future supply of energy. Indeed, many scientists and researchers have been worried about the depletion of fossil fuel and severe pollution issues were caused by the combustion of fossil fuels, especially occurred in many developing countries. Thus, an efficient renewable resource has been introduced by producing clean hydrogen fuel via photocatalytic water splitting process [1,2]. This approach has been received a great interest in the development of sustainable and economic way for the production of H<sub>2</sub> lately. In order to bring H<sub>2</sub> to the point of commercial readiness and establish H<sub>2</sub> economy, substantial research on the development of advanced hybrid nanocomposite film for photocatalytic water splitting process using our solar energy has been developed lately[3, 4]. Although a number of nanocomposite film have been reported to be active photocatalysts for the overall photocatalytic water splitting reaction, most of them only function under ultraviolet illumination owing to the wide band gap energy level. Since nearly half of the solar energy incident on the earth's surface falls in the visible region (400 <  $\lambda$  < 800 nm), therefore, the efficient use of visible light from our solar energy is essential in H<sub>2</sub> gas generation through photocatalytic water splitting process [5, 6]. Unfortunately, overall photocatalytic water splitting using our solar energy is difficult to achieve due to the band gap energy level for most of the nanocomposite film is rather difficult to be tuned to visible region (small band gap energy level) [7, 8]. To date, no known nanocomposite film has been discovered that simultaneously meets all the basic criteria required for economical H<sub>2</sub> production via photocatalytic water splitting process [4]. In fact, a suitable candidate as a photoelectrode in

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water splitter cell for H<sub>2</sub> production must have three basic criteria, including the high stability in aqueous solution, smaller band gap energy level, as well as the oxidation and reduction potential of respective nanocomposite film must lie between the valence and conduction band edges [9].

Since the first report by Fujishima and Honda on the photocatalytic water splitting reaction on a TiO<sub>2</sub> photoelectrode, the advanced photocatalytic oxidation technology has become a promising way to generate a clean, low-cost, and environmentally friendly H<sub>2</sub> gas by utilizing our solar energy [10]. Many scientific studies of TiO<sub>2</sub> have been established and published in the late of 20th century due to its unique physio-chemical properties. To date, one-dimensional (1D) structure of highly ordered TiO<sub>2</sub> nanotubes on a titanium film by using electrochemical anodization technique under a specific set of environment conditions has been widely reported. Nevertheless, 1D TiO<sub>2</sub> nanotubes film is still far from becoming a potential candidate for photocatalytic water splitting application. The main drawbacks are poor visible-light absorption and high recombination losses of charge carry [11]. In fact, pure TiO<sub>2</sub> nanotubes film can only effectively work with photocatalytic response under UV region ( $\lambda < 400\text{nm}$ ). In general, our solar energy only contain about 4-5% of UV rays, which is further slowdown the photocatalytic response using pure TiO<sub>2</sub> nanotubes film [4]. Thus, utilization of visible light from our solar energy (40-45%) is essential that lead to the higher photoconversion efficiency in solar-driven water-splitting applications. Continuous efforts have been carried out by simultaneous control of oxidation and dissolution reactions to grow highly-ordered nanotube arrays on titanium film by incorporating an optimal content of adsorbed small band gap energy level dopant - cadmium-selenide (CdSe). Theoretically, CdSe is one of the most popular II-VI semiconductor materials to be used to sensitize the wide band gap nanocomposite film due to its wider absorption range (below 730 nm). In this case, an advanced hybrid nanocomposite film with large extinction coefficient strongly absorb visible light can be created at where the conduction band edge level of a small band gap CdSe species is located at higher position than that of the TiO<sub>2</sub> itself. As a result, more photo-generated electrons in the small band gap CdSe could be injected to the conduction band of the TiO<sub>2</sub> effectively with high transportation rate and minimal recombination losses. Thus, higher photocatalytic water splitting response to reduce more hydrogen ions into hydrogen gas could be expected [12-14]. Making intuitive guesses on their properties are more or less impossible, and a focused research on the area is a very challenging task. Thus, a hybrid of CdSe - TiO<sub>2</sub> nanocomposite film, acting as a photoelectrode in photocatalytic water splitter system has been developed in our study. The novelty of this work is to obtain a desired hybrid nanocomposite film, resulting in high photocatalytic water splitting performance under solar illumination as compared to the pure TiO<sub>2</sub> nanotubes film.

## 2. MATERIAL AND METHODS

CdSe species loaded TiO<sub>2</sub> nanotubes film via chemical bath deposition technique was carried out. 99.6% purity of Ti foil with thickness of 0.127 mm from STREM Chemicals was applied in this experimental work. Ti foil was cut into desired dimension (50 mm × 20 mm). First, Ti foil was degreased with ultrasonic for 30 min in both acetone and ethanol. Then, Ti foil was then placed in an electrolyte consisting of ethylene glycol with 0.5 wt% ammonium fluoride and 5 wt% of hydrogen peroxide. Electrochemical anodization experiment was performed in a two-electrode configuration bath with Ti foil served as the anode and a platinum rod served as the cathode. Then, as-anodized Ti foil was cleaned by using distilled water and acetone then dried in atmosphere. Based on our previous studies, anatase crystalline phase of TiO<sub>2</sub> is the most desirable structure that exhibit a higher photocatalytic water electrolysis response as compare to rutile crystalline phase TiO<sub>2</sub> [15-17]. In this study, calcination temperature at 400 °C for 4 hours in the air atmosphere was conducted in order to convert the amorphous phase of TiO<sub>2</sub> nanotubes into the crystalline anatase phase before carrying out next doping experimental work. Then, cadmium acetate Cd(CH<sub>3</sub>COO)<sub>2</sub> solution was added slowly with ammonia solution

with constant stirring for deposition of CdSe species on TiO<sub>2</sub> nanotubes film. Next, Na<sub>2</sub>SeSO<sub>3</sub> solution was then added slowly to the mixture solution with constant stirring. The resultant pH of the final solution was around 12-12.5. In this case, the bath mixture solution has kept at room temperature without stirring. The substrates coated with CdSe species was removed and rinsed in double distilled water, and dried in air.

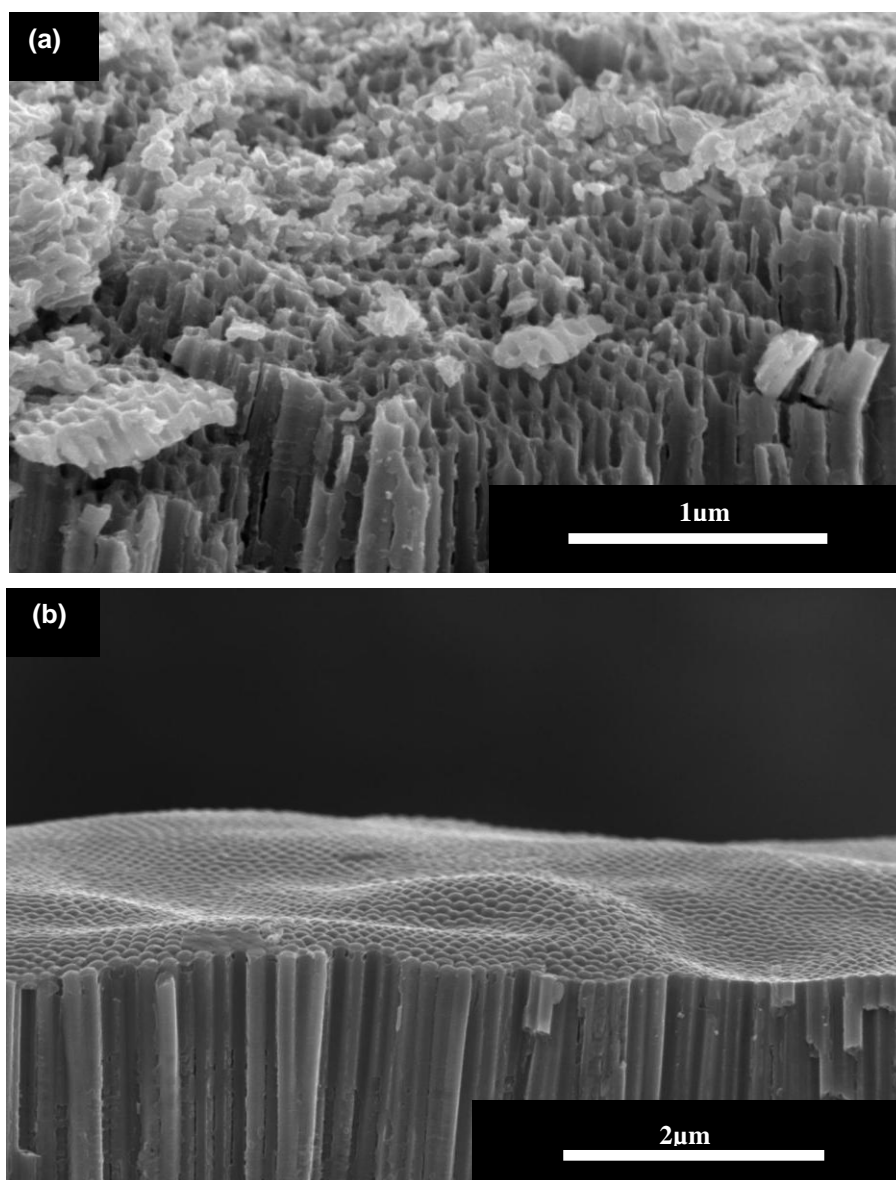
The surface and cross-sectional morphologies of the samples were observed via field emission scanning electron microscopy (FESEM) using JEOL JSM 7600-F operated at 5 kV and 10 kV with working distance of approximately 1 mm, whereas the element analysis was performed by Energy Dispersive X-ray Spectroscopy (EDX) analysis with an Oxford Instruments. XRD (Bruker AXS D8 Advance, Germany) analysis was conducted using a Cu target (Nickel filter), K $\alpha$  radiation ( $\lambda = 0.1546$  nm) at scanning rate over angle,  $2\theta$  in the range 20 - 70°. Next, photocatalytic water electrolysis response for both pure TiO<sub>2</sub> nanotubes and CdSe species loaded TiO<sub>2</sub> nanotubes film were determined by using three-electrodes electrochemical water electrolysis system (150 ml in volume) at where our synthesized nanocomposite film served as working photoelectrode, a platinum rod served as the counter electrode and a saturated calomel electrode (SCE) served as the reference electrode. All of the three electrodes were connected to a potentiostat ( $\mu$ Autolab III) with a 150 W xenon lamp (Zolix LSP-X150) as illumination source. The evolved hydrogen gas was collected using a reverted burette. As the H<sub>2</sub> gas is produced in counter electrode in water electrolysis system, it will bubble up into inverted burette. The volume of gas is determined by reading the gas level on the side of burette. The overall photoconversion efficiency ( $\eta$ ) is defined as the ratio of maximum energy output that can be obtained from the final products to the energy supplied in the form of light to produce them. The maximum  $\eta$  (the light energy to the chemical energy conversion efficiency) was calculated as follows:

$$\begin{aligned}(\eta) &= [(total\ power\ output - electrical\ power\ output)/light\ power\ input] \times 100\% \\ &= j_p [(E_{rev}^0 - |E_{app}|) / I_0] \times 100\end{aligned}$$

where  $j_p$  is the photocurrent density (mA/cm<sup>2</sup>),  $j_p E_{rev}^0$  is the total power output,  $j_p |E_{app}|$  is the electrical power input,  $I_0$  is the power density of the incident light (mW/cm<sup>2</sup>),  $E_{rev}^0$  is the standard reversible potential (1.23 V/SHE), and  $E_{app} = E_{mean} - E_{aoc}$ . In this equation,  $E_{mean}$  is the electrode potential (versus SCE) of the working electrode where the photocurrent was measured under illumination and  $E_{aoc}$  is the potential (versus SCE) of the working electrode at open-circuit condition.

### 3. RESULTS AND DISCUSSION

FESEM micrographs of TiO<sub>2</sub> nanotube surfaces after soaking at precursor's molarity of 5 mM for 1 h were shown in Figure 1 and the EDX analysis was summarized in Table 1. As shown in the Figure 1(a), top view of CdSe loaded TiO<sub>2</sub> nanotubes film revealed similar opening tubular structure to the pure TiO<sub>2</sub> nanotubes. The bottom view of the CdSe loaded TiO<sub>2</sub> nanotubes, which are in the form of domes is called barrier layer with typical shape of hexagonal or pentagonal is presented in Figure 1(b). Nevertheless, the resultant TiO<sub>2</sub> nanotube arrays were extensively covered by aggregated CdSe nanocluster with approximately 1.19 at % of Cd content and 1.06 at% of Se content, respectively. The tubes have an average diameter of 150 nm, length of 5  $\mu$ m, and wall thickness of 30 nm. It was believed that aggregated CdSe nanocluster was triggered by higher ionic product (Cd and Se ions) than the solubility product (CdSe solid phase). Thus, it caused rapid formation of ion-by-ion condensation of the Cd<sup>2+</sup> and Se<sup>2-</sup> or by adsorption of colloidal particles from the solution on the TiO<sub>2</sub> nanotubes [18, 19].



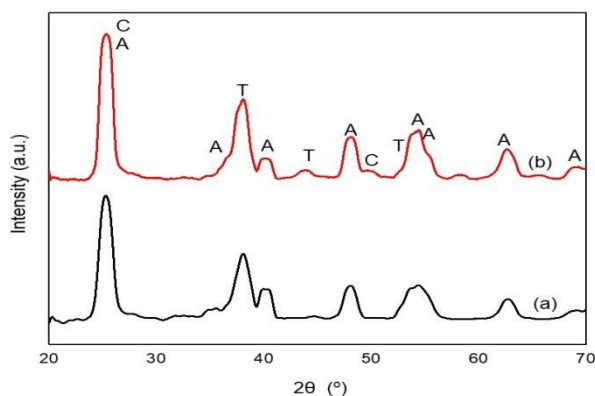
**Figure 1.** FESEM images of CdSe loaded TiO<sub>2</sub> nanotubes film, (a) Top view, (b) cross-section bottom view.

**Table 1** Average at% of pure TiO<sub>2</sub> nanotubes and CdSe loaded TiO<sub>2</sub> nanotubes film obtained by EDX analysis

Sample	Ti (at%)	O (at%)	Cd (at%)	Se (at%)
Pure TiO <sub>2</sub> sample	38.46	61.54	-	-
CdSe loaded TiO <sub>2</sub> sample	39.97	57.78	1.19	1.06

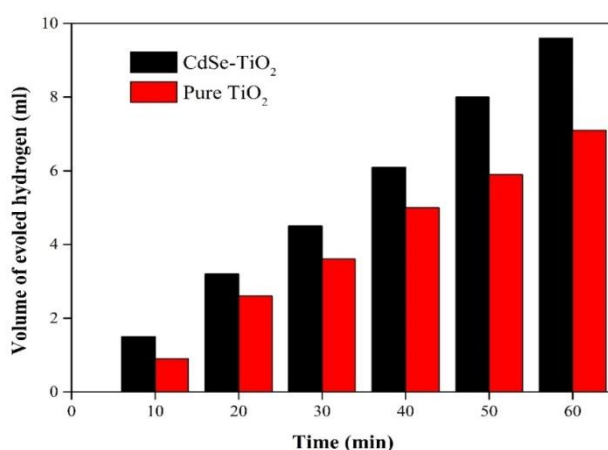
Figure 2 shows the XRD diffraction patterns of pure TiO<sub>2</sub> nanotubes and CdSe loaded TiO<sub>2</sub> nanotubes film. Diffraction peaks attributed to the anatase phase of TiO<sub>2</sub> were detected. It could be observed that diffraction peaks at 25.37°, 38.67°, 48.21°, 54.10°, 55.26°, 62.66° and 68.74° are corresponding to (101), (112), (200), (105), (211), (204) and (116) crystal planes of the TiO<sub>2</sub> anatase phase, respectively. Besides the peaks coming from anatase phase of TiO<sub>2</sub>, there also diffraction peaks from Ti substrate at 35.1°, 38.4°, 40.2° and 53.0°, which correspond to the crystal planes of (100), (002), (101) and (102) respectively. Interestingly, all the diffraction peaks are indexed to anatase phase of TiO<sub>2</sub> and Ti metal itself indicating the incorporation of CdSe species did not change the lattice structure of pure TiO<sub>2</sub> nanotubes significantly [19-20]. However, the XRD pattern for the sample of CdSe loaded TiO<sub>2</sub> nanotubes film small

characteristic diffraction peak of cubic zinc blended phase CdSe at  $49.7^\circ$  which respective to crystal plane of (311). Moreover, an obvious increase in intensity of the peak at  $25^\circ$  was vaguely observed. This is due to overlapping of the peak of (111) plane ( $25.35^\circ$ ) of cubic phase CdSe and the peak of (101) planes of anatase  $\text{TiO}_2$ . These results infer that CdSe species did not enter into the crystal lattices of  $\text{TiO}_2$  and instead covered the opening mouth surface of  $\text{TiO}_2$  nanotubes as presented in Figure 1(a).



**Figure 2.** XRD patterns of (a) pure  $\text{TiO}_2$  nanotubes and (b) CdSe loaded  $\text{TiO}_2$  nanotubes (A = anatase, T = Titanium, C = CdSe).

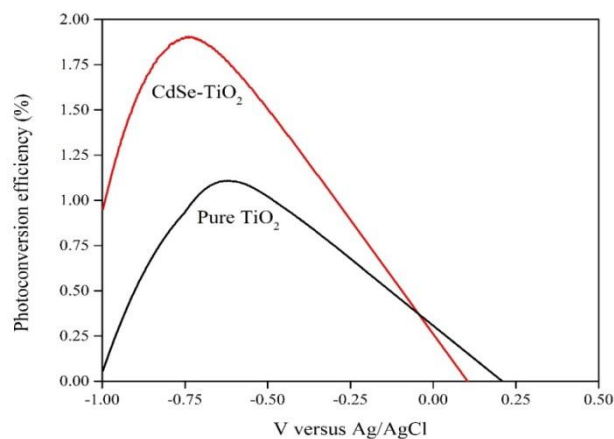
Next, evolution rate of  $\text{H}_2$  gas generated from the photocatalytic water-electrolysis process was evaluated (Figure 3). It was noticed that  $\text{H}_2$  generation rate was increased linearly with increasing exposure time. The hybrid nanocomposite film subjected to 5 mM CdSe precursor achieved a maximum evolution of 9.6 ml, which was relatively higher compared with pure  $\text{TiO}_2$  nanotubes (7.1 ml). Based on our data collection,  $\text{H}_2$  generation rate for CdSe-loaded  $\text{TiO}_2$  nanotubes film and pure  $\text{TiO}_2$  nanotubes film are 3.2 and 2.78  $\text{mL}/\text{cm}^2\text{h}$ , respectively. This reveals that the hybrid nanocomposite system nanotubes exhibited better charge carrier transfer properties, and thus generating more  $\text{H}_2$  gas at counter electrode of platinum rod.



**Figure 3.** Comparison of  $\text{H}_2$  evolution using advanced hybrid nanocomposite – CdSe-loaded  $\text{TiO}_2$  nanotubes film and pure  $\text{TiO}_2$  nanotubes film under 150 W solar simulator for 60 min.

Meanwhile, photoconversion efficiency,  $\eta$  also has been conducted to estimate the correlation of light absorption quantitatively. Based on the Figure 4, the  $\eta$  curve of CdSe- $\text{TiO}_2$  nanotubes film gives the highest  $\eta$  of about 1.9% which compare with  $\eta$  of pure  $\text{TiO}_2$  is about 1.1%. The main reason was attributed to the sufficient amount of CdSe nanoclusters deposited on the surface of  $\text{TiO}_2$  nanotubular structure, which able to improve both the light absorption and contact degree with the water for better photocatalytic water electrolysis response. More excited electrons

from CdSe nanoclusters could quickly transfer to the TiO<sub>2</sub> nanotubes film's surface and then further reduced more hydrogen ions into hydrogen gas [8]. This result was in line with the photoconversion efficiency. The H<sub>2</sub> generation was completely stopped after the termination of solar irradiation. This observation was a clear indication that H<sub>2</sub> is only produced photocatalytically via water electrolysis process. A constant production rate of H<sub>2</sub> gas was found in the present study.



**Figure 4.** The  $\eta$  curves of advanced hybrid nanocomposite – CdSe-loaded TiO<sub>2</sub> nanotubes film and pure TiO<sub>2</sub> nanotubes film under 150 W solar simulator for 60 min.

#### 4. CONCLUSION

The present work clearly to show that advanced hybrid nanocomposite – CdSe-loaded TiO<sub>2</sub> nanotubes film showed an great improvement in photocatalytic water electrolysis performance than that of the pure TiO<sub>2</sub> nanotubes film. An optimum content of CdSe species (~1 at%) on TiO<sub>2</sub> nanotubes demonstrated a maximum photoconversion efficiency of 1.9 % with hydrogen gas evolution rate of 3.2 mL/cm<sup>2</sup>h under solar illumination. This is ascribed to an effective separation of charge carriers and greatly reduces the recombination losses within the advanced hybrid nanocomposite – CdSe-loaded TiO<sub>2</sub> nanotubes film. Such mechanistic understanding and findings is very important for improving the hydrogen generation via water splitting process, which may be used to realize the pollution-free hydrogen economy in our near future.

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