ASSESSING THE EFFECTS OF SENSITIZING TUNGSTEN OXIDE WITH ZINC TELLURIDE

BY
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This thesis is a comparison study of the performance of plain tungsten oxide (WO$_3$) thin films and tungsten oxide thin films sensitized with zinc telluride (ZnTe) as photoelectrocatalysts. Tungsten oxide and zinc telluride are semiconductors which were prepared on indium tin oxide (ITO) coated glass, and subsequently studied for water splitting applications. The main method of synthesis employed was electrochemical deposition. Tungsten oxide thin films were deposited from a precursor solution of peroxotungstic acid while the zinc telluride thin films were deposited from a solution containing dissolved zinc sulfate heptahydrate, sulfuric acid and tellurium dioxide. Surface morphology, film composition and electrochemical properties were investigated using scanning electron microscopy, (SEM), energy dispersive spectroscopy (EDS), and electrochemical impedance spectroscopy, (EIS) respectively. The sensitization of WO$_3$ using zinc telluride showed an improvement in the water splitting capabilities of the thin films as shown by the chronoamperometry curves.
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Dedication

This thesis work is dedicated to my mother, Eunice Madya Kazuva for showing me the true meaning of strength in her fight against cardiomyopathy.
Chapter 1
Introduction

A consistent increase in the adverse effects of global warming throughout the years has made the need for renewable sources of energy more apparent. Energy demands have been on an increasing trajectory with a projected 56% increase between 2010 and 2040 as reported by the U.S Energy Information Administration. The largest energy supply is oil which provides about 40% of the total energy requirements. As such there is a prevalent risk of an increase in greenhouse gas emission into the atmosphere from fossil fuel exploitation.

Different countries have injected up to millions of dollars’ worth of funding into renewable energy research institutions. Hydrogen production from water splitting has been the most promising so far merely due to the abundance of water in oceans and the potential of harnessing the untapped solar potential (120,000 TW) [1]. Hydrogen has the highest energy density amongst common energy storage materials. The only product of its combustion is water which is environmentally friendly unlike other greenhouse gases.
In 1969 Fujishima and Honda gave a new and different scope to hydrogen production when they reported a successful water photoelectrolysis experiment with the use of a photosensitive semiconductor, titanium dioxide for the very first time [1,2]. Titanium dioxide, however, has a very large bandgap of 3.2 eV; hence it absorbs within the ultraviolet region ($\lambda \leq 387$ nm) therefore, the splitting was achieved under ultraviolet illumination [2]. As such, only 5 % of the solar energy can be utilized using this material because the ultraviolet region radiation is 4-5% of the solar spectrum. The visible light (white light) of the solar spectrum which constitutes the bulk of the solar radiation that reaches the earth’s surface has wavelengths between 400 - 700 nm (1.8 - 3 eV).

Figure 1: World’s total energy consumption distribution
Consequently, researchers have since studied and in other instances modified a lot of semiconductors in an attempt to come up with a perfect catalyst that results in improved visible light absorption, reduced charge recombination rate and efficient utilization of the abundant solar energy. This has been done through tailoring the bandgap of semiconductors by changing the relevant synthesis parameters [3-6].

An ideal semiconductor for photocatalysis, should not only exhibit high photoactivity, but it should be durable in aqueous medium and show resilience to photocorrosion [1]. This material should also have a relatively small bandgap that allows for utilization of the visible light and infrared section of the solar spectrum which when combined make up almost 95% of the radiation that reaches the earth’s surface. Photoexcited charges must be separated efficiently to avoid recombination and they must have sufficient energy to carry out the desired water splitting reactions [1]. Photosensitization occurs when a material that absorbs light energy, transforms this energy into chemical energy, then transfers it to otherwise photochemically unreactive or less reactive substrates under specific conditions [2]. Normally, the photosensitizer is coated onto the surface of the substrate to be sensitized, and upon excitation the photosensitizer injects
electrons into the conduction band of the substrate. The most common photosensitizers that have been studied and proven to be effective are inorganic sensitizers, organic dyes and coordination metal complexes [3].

**Motivation of study**

Tungsten oxide and ZnTe are two of the few semiconductors which have exhibited high photoactivity and electrochromic capabilities as reported by other researchers over the past two decades in the search for durable materials for hydrogen (H₂) production from photoelectrochemical water (H₂O) splitting. The optical bandgap of WO₃ has been reported to be in the range 2.6 to 2.8 eV (476-442 nm) [2,3]. The conduction and valence band edges are located at -0.3 and 2.4 V, respectively, making it an excellent candidate for achieving water splitting using visible light [2]. This material also has high stability such that it is not susceptible to photocorrosion unlike other semiconductors. Tungsten oxide thin films have a wide range of applications in microelectronics and optoelectronics, dye sensitized solar cells, visible light promoted photodegradation of the contaminants, colloidal quantum dot light-emitting diodes and most importantly for this investigation, water splitting photo catalysis [3, 7, 19]. There is no single semiconductor catalyst for effective photoelectrochemical water splitting thus previous literature has
shown an advancement which involves the combination of two semiconductors to improve performance of the catalyst [4].

Figure 2: Proposed mechanism for sensitized photocatalysis under visible light radiation, including forward electron transfer (solid lines) and possible recombination pathways (dotted lines). Copy from [1]. Copyright 2009 American Chemical Society.

Pei and Luan described the development of visible light responsive sensitized photocatalysts for semiconductors such as TiO$_2$, ZnO, Fe$_2$O$_3$, CdS and ZnS [3]. The scheme in Figure 2 illustrates possible recombination pathways and fluorescent decay of an excited sensitizer. In the photosensitization system shown above dye S is both the sensitizer and molecular bridge between electron donor D to the metal oxide semiconductor. The visible light (>400nm) with the energy which is lower than
the band gap of the semiconductor photocatalyst but higher than the band gap of the sensitizer molecules (S) which are adsorbed on the photocatalyst excites the sensitizer, and subsequently the electrons are injected to the conduction band (CB) of the photocatalyst, leading to the efficient charge separation at the interface between the photocatalyst and the sensitizer and producing the oxidized form of the dye (S$^+$). Subsequently the electrons can reduce water to H$_2$ on the reduction site (Pt mostly) over the photocatalyst in the process of water splitting [3].

A high quantum yield is only possible when the forward electron transfer rate (solid lines) is faster than the rate of all the reverse rates (doted lines) from the same point in the system [1,8]. Mostly, the reverse pathways have much greater driving forces than forward ones resulting in limited hydrogen production. In this study, there exists an interface between the catalyst (WO$_3$) and the sensitizer (ZnTe) which decreases the susceptibility for recombination of the separated charges.

The core of each industry is the financial feasibility of a process and its ability to give a return of the capital invested. It is important to find suitable methods allowing for its easy and inexpensive large scale production. The electrodeposition method is simple, inexpensive and operates at low pressure and temperature which eliminates the use of high pressure autoclaves and highly acid resistive liners in the reaction chambers as is the
case with other synthesis methods. It also allows for coating larger surface areas with good potential for controlling film thickness unlike other synthesis methods such as sol-gel deposition, hydrothermal, thermal vapor deposition, and spin coating, among others [3,7,10]. It has been reported that sol-gel synthesis with tungsten alkoxides resulted in porous films that had excessive carbon impurities [3]. Electrodeposition was also favorable in this study because some sensitizers have a problem of dissolution and washing away in solution if they are simply sprayed onto substrates. Electrodeposited thin films that adhere well to the ITO glass substrates are more stable in that aspect.
Chapter 2
Objective of Study

The main objective of this research is to sensitize tungsten oxide with another semiconductor, zinc telluride, ZnTe and observe the effects of doing so with regards to the performance of the composite electrode as a photocathode for hydrogen production. Although organic dye sensitizers such as cyanine, rinoflavina and cresyl violet have been studied the most compared to other sensitizers due to their low cost, low toxicity and easy handling approaches, their stability is an apparent problem that cannot be ignored [2]. In light of the capabilities of semiconductors, the ones with narrow bandgaps that can adsorb visible light have also been studied as potential sensitizers. They are an attractive route to improved sensitization due to their stability and adjustable bandgaps as opposed to organic dyes.

The successes of dye sensitization suggest that another metal compound, in this case ZnTe, which has an appropriate bandgap alignment for high utilization of the visible light of the solar spectrum can be used as a sensitizer as well. A metal based sensitizer would work in a similar fashion to dye sensitizers, however, with improved stability against photo corrosion in stark contrast to dyes. The fact that ZnTe has not been studied in detail in conjunction with WO₃ usage, makes it an interesting candidate of study in
improving the performance of WO$_3$ as a photocathode for H$_2$ production. This material has a relatively narrow bandgap of 2.26 eV (548 nm) for effective light harvesting and its conduction band edge positioned at -1.63 eV offers a large driving force for interfacial electron transfer from the semiconductor to the WO$_3$ acceptor [22].
Chapter 3
Literature Review

Giannouli and Leftheriotis [8] described the cathodic electrodeposition of WO$_3$ from peroxotungstic acid which was first reported by Yamanaka et al [25]. The predominant peroxotungstate in the precursor solution is the dimer $W_2O_{11}^{2-}$ which is formed by the dissolution of tungsten metal in concentrated hydrogen peroxide as shown below [2]:

$$2W + 10H_2O_2 \rightarrow W_2O_{11}^{2-} + 2H^+ + 9H_2O$$

(1)

This dimeric species is the reason why the obtained solutions are highly acidic. However, the formed peroxotungstates are thermodynamically unstable and decompose slowly yielding a tungsten trioxide precipitate according to the reactions [2]:

$$W_2O_{11}^{2-} + 2H^+ \rightarrow 2WO_3 + 2O_2 + H_2O$$

(2)

$$6W_2O_{11}^{2-} + 6H^+ \rightarrow W_{12}O_{39}^{6-} + 12O_2 + 3H_2O$$

(3)

For this reason, ethanol or isopropanol is added in order to improve the stability of the peroxotungstic acid [7]. During the cathodic electrodeposition, the peroxotungstic dimer undergoes reduction to tungsten trioxide.
A very important aspect of this paper is the report on the effect of aging on the precursor solution.

This aforementioned solution was used for several depositions at different time intervals ranging from 1 to 122 h after the precursor formation. Film thickness and diffusion coefficient increased with increasing aging time of the precursor solution.

Shahizuan and Mohd [15] reported a synthesis method similar to that done by Yamanaka et al [25]. However, in their report, they investigated the influence of pH on the electrodeposition of tungsten oxide. A decrease in pH to about 0.8 resulted in faster nucleation and growth of WO$_3$ and this resulted in a thicker and denser mesoporous film compared to deposition at higher pH values. Deposition at higher pH values resulted in smooth thin films. This is clearly noticeable on the SEM images provided. At higher pH values there is an excess of H$^+$ ions close to the electrode leading to a quick deposition according to Equation 2 indicated above.

Table 1 gives a summary of the differences in the appearance of deposited films and precursor solutions at different pH values. Similar results were also observed when pH values of precursor solution was varied.
Table 1: Characteristics of the deposition solution containing 0.05M Na$_2$WO$_4$.2H$_2$O plus 5 mL H$_2$O$_2$ with the presence of different amount of nitric acid [8].

<table>
<thead>
<tr>
<th>Solution pH</th>
<th>Color</th>
<th>Solution appearance</th>
<th>WO$_3$ films formed as observed by FESEM</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.8</td>
<td>very light yellow</td>
<td>No color change</td>
<td>Only a few particles of deposited WO$_3$</td>
</tr>
<tr>
<td>1.3</td>
<td>light yellow</td>
<td>Fine and small particles of WO$_3$ in solution</td>
<td>All surface covered by a smooth thin film</td>
</tr>
<tr>
<td>0.8</td>
<td>Milky yellow</td>
<td>Colloidal suspension, the formation of yellow sediment at the bottom of the container is left unstirred</td>
<td>All surface covered by a porous and thick film</td>
</tr>
</tbody>
</table>

After employing the synthesis method employed by Yamanaka, M.Deepa, et al annealed the films at different temperatures and reported the observed differences in the morphologies of these films [13]. Films that were annealed at temperatures between 60 to 100 °C were characterized by nanosized grains coexisting with a nanoporous amorphous structure. These films had high porosity and the open structure ensured high transmission modulation, coloration efficiency, high charge capacity, and fast color-bleach kinetics. The films annealed at 400 and 500 °C had triclinic and hexagonal crystalline structures. These films exhibited poor performance due to the
preponderance of the crystalline structure and a dense microstructure. This study concluded that the grain size increases while the pore size decreases as temperature increases as shown in Table 2 below. Anodic peak current, bleaching and coloration charges decrease as annealing temperature increases as a result of the structure of the films being less open and porous.

**Table 2: Variation of electrochemical properties of WO$_3$ films as a function of annealing temperature [13].**

<table>
<thead>
<tr>
<th>Annealing temperature ($^\circ$C)</th>
<th>Anodic peak current (mA)</th>
<th>Coloration charges</th>
<th>Bleaching charges</th>
<th>Diffusion coefficient (cm$^2$/s)</th>
<th>Grain size (nm)</th>
<th>Pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>23</td>
<td>17.6</td>
<td>$3.4 \times 10^{-10}$</td>
<td>10-20</td>
<td>2-25</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>3.3</td>
<td>21.2</td>
<td>19</td>
<td>$6.08 \times 10^{-10}$</td>
<td>15-25</td>
<td>4-16</td>
</tr>
<tr>
<td>100</td>
<td>0.97</td>
<td>12.5</td>
<td>9.0</td>
<td>$5.9 \times 10^{-11}$</td>
<td>20-30</td>
<td>4-8</td>
</tr>
<tr>
<td>250</td>
<td>1.85</td>
<td>8.5</td>
<td>7.0</td>
<td>$1.7 \times 10^{-10}$</td>
<td>12-32</td>
<td>8-12</td>
</tr>
<tr>
<td>400</td>
<td>1.6</td>
<td>5.4</td>
<td>4.85</td>
<td>$1.3 \times 10^{-10}$</td>
<td>13-52</td>
<td>6-10</td>
</tr>
<tr>
<td>500</td>
<td>1.3</td>
<td>3.5</td>
<td>3.2</td>
<td>$8.1 \times 10^{-1}$</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

S. A. Mohamad, et al [26] described the controlled electrodeposition and characterization of ZnTe. The first stock solution contains dissolved
zinc sulfate in deionized water while the other consists of tellurium dioxide dissolved in deionized water with the aid of a few sulfuric acid droplets. This procedure is as reported in previous works reported by S.A Mohamad, et al [26] and Takahiro Ishizaki, et al [27]. The deposition of ZnTe is in two parts the underpotential reduction of HTeO$_2^+$ ion to Te and water, and the cathodic reduction of Zn$^{2+}$ ions in solution to Zn as shown in the equations below:

\[
HTeO_2^+ (aq) + 3H^+(aq) + 4e^- \rightarrow 2H_2O(aq) + Te(s)
\]  

(4)

\[
Zn^{2+}(aq) + Te(s) + 2e^- \rightarrow ZnTe(s)
\]

(5)

Crystalline films were obtained at a deposition potential of -0.9 V and bath temperature of 98°C using a large [Zn$^{2+}$] to [HTeO$_2^+$] concentration ratio at pH 3.0. More cathodic potentials caused hydrogen evolution which deterred film formation whilst lower cathodic potentials caused irregular film growth.
Chapter 4
Method of Research

This study employed the use of a potentiostat to perform electrodeposition of films and investigate the electrochemical properties of the prepared films. Different types of characterization methods were also used in order to determine the surface morphology, composition and crystallinity (if any) of the films. In-depth knowledge of redox reactions, cell potentials, electrolytic cells, electrolysis and electrodeposition was very vital in order to successfully complete this project. This project also encompassed general chemistry, quantum physics and a background on catalyst functionalities. In addition to the principles above, materials characterization is vital especially scanning electron microscopy, transmission electron microscopy, x-ray diffraction, energy dispersive spectroscopy, and electrochemical impedance spectroscopy, among others. These characterization methods can provide more information on surface morphology, grain sizes, porosity, crystallinity,
Electrodeposition of WO$_3$ thin films

To start the experiment, 4 mL of water, 6.5 g of tungsten powder and 40 mL of hydrogen peroxide, H$_2$O$_2$ (30% concentration) were each placed in clean glassware as described in [5]. All chemicals were obtained from Sigma Aldrich. A 250 mL conical flask containing the measured out 40 mL of hydrogen peroxide and 4 mL of water was placed in an ice bath. Tungsten powder was added in small amounts under continuous agitation at temperatures between 0 and 5 °C because the reaction is exothermic. This was done for 30 minutes and the mixture was placed in a refrigerator at 2 °C to give ample time for the tungsten powder to dissolve. After four days, all the tungsten powder had dissolved and a clear, slightly yellowish solution was obtained.

This solution had excess hydrogen peroxide to keep it stable during dissolution, however, the excess H$_2$O$_2$ impedes the electrodeposition process if kept in solution. A very small amount of platinum black was added to the PTA solution to catalytically decompose excess hydrogen peroxide at 50 °C and continuous agitation [8,13]. Right after adding platinum black a lot of fizzing and effervescence was observed due to the rapid evolution of oxygen gas. The fizzing died down after 1 h of agitation which showed that all the H$_2$O$_2$ had decomposed. This process yielded a milky yellow solution with small fine suspensions. The platinum black was filtered out and the
solution was mixed with equal volumes of anhydrous absolute ethanol and water. Ethanol was used to stabilize the peroxotungstates which are thermodynamically unstable complexes. It has been reported that aging the precursor solution for a few days before use yields films of better uniformity and thickness in comparison to films from unaged solutions, hence the solution was left to age for 3 days before use. The pH of this precursor solution was also reduced by adding a few droplets of hydrochloric acid. Lower pH values have proven to improve electrodeposition of WO$_3$ thin films as reported by Shahizuan and Mohd [15]. The excess H$^+$ ions in solution on the cathode surface favor the forward reaction that results in the deposition of WO$_3$ thereby improving the deposition rate. All pH and temperature measurements were done using the H12211pH benchtop meter by Hanna Instruments.

The cathode, ITO coated glass secured from Delta Technologies was cleaned by consecutive sonication in DI water, acetone, isopropanol and ethanol prior to use. Electrodeposition was carried out under potentiostatic condition using the Gamry Interface 1000 with Dr. Bob’s cell of volume 30 mL (shown in Figure 5). A chronoamperometric deposition was done at a constant potential of -0.45 V for 300 s under ambient conditions using a three-electrode configuration, consisting of Pt a counter electrode, Ag/AgCl reference electrode, and ITO coated glass with dimensions 5x100x1.1 mm...
as a working electrode. During deposition, the effective immersion area of ITO coated glass was fixed constant at 1.1 x 10 mm. After deposition, the electrode was first placed in equal parts deionized water-ethanol mixture for 2hr to remove excess electrolyte before being left to dry overnight [18].

**Electrodeposition of ZnTe thin films**

The WO$_3$ thin films on ITO coated glass prepared above were further modified through surface electrodeposition of ZnTe. All chemicals were obtained from Sigma Aldrich and were used without further purification. The working solution of tellurium dioxide, TeO$_2$ was prepared by dissolving 20 mg of TeO$_2$ in 250 mL of ~ 18 megaohm deionized water. To improve the rate of dissolution of TeO$_2$ in water, 5 mL of 98% concentrated sulfuric acid was added to the working solution and this was heated at 70°C under continuous stirring for 1 h. The zinc sulfate heptahydrate, ZnSO$_4$.7H$_2$O stock solution was prepared by dissolving 10.8 g of ZnSO$_4$.7H$_2$O in 250 mL of distilled water. The final precursor solution consisted of equal volumes of the two working solutions. Electrodeposition of ZnTe on top of WO$_3$ thin films was done using the Gamry Analyst Interface 1000 under potentiostatic settings. The effective immersion area of ITO coated glass was maintained at 1.1x10 mm during deposition. The electrodeposition was done using
chronamperometry at a temperature of 98 °C, pH of 3.7 and constant voltage of -0.75 V. Due to the existence of WO₃ thin films, on the ITO substrate, the adhesion of ZnTe can be compromised at temperatures lower than 98 °C and pH values lower than 3.7. At lower pH and temperature values, only zinc was deposited on to the electrode surface. The 0.75 V encouraged fast deposition time which deterred intercalation of all the positive ions in solution into the porous structure of WO₃. At more negative potentials, there was a significant reduction in deposition of ZnTe since a side reaction yielding hydrogen gas was favored more.

Some of the composite electrodes prepared using the method above were further modified by adding a protective carbon layer. The carbon layer would then improve the stability of the electrode against photocorrosion and improve electron movement at the electrode/electrolyte triple phase boundary due to its high conductivity.

This carbon layer was synthesized using the wet chemical method as reported by Jang, et al [22]. Equal amounts of glucose solution of a known concentration, (5 mg/mL) were pipetted onto the coated surface of the ITO substrates and left to dry overnight. These were annealed at 450°C for 5 h in a tube furnace under a continuous helium flow and this yielded a smooth visible carbon layer. Exposing the ITO glass substrate to high temperature reduced its electrical conductivity. Furthermore, the morphology of the WO₃
thin films changed from amorphous to triclinic at temperatures above 400°C. 

Deepa, et al report that at temperatures above 400°C, the grain size of WO₃ almost doubles and the pore size decreases by a factor 3 [13]. The crystallinity of the films at elevated temperatures increases at the expense of film porosity and subsequently film surface area.
Chapter 5
Results and Discussion

Studies on WO₃ thin films

Figure 3: Cyclic voltammetry sweep of ITO in peroxotungstic acid (WO₃ precursor solution)

The voltammogram of WO₃ (Figure 3) shows a reduction peak close to -0.45 V which is the reduction of peroxotungstic acid to tungsten oxide on the surface of the electrode. The potential at which reduction occurred was used as the electrodeposition potential of the WO₃ thin films. This was
consistent with what was reported in literature. It is important to note that the potentiostat settings were such that a positive current represented reduction.

**Figure 4:** Stable current during the chronoamperometric deposition of WO$_3$ thin films at 25 °C

Tungsten oxide was electrodeposited at a constant current of about 1 mA. This current increased at lower pH values. At higher pH values, there is an excess of H$^+$ ions close to the electrode leading to a quick deposition according to equation
\[ W_2O_{11}^{2-} + 2H^+ \rightarrow 2WO_3 + 2O_2 + H_2 \] (2)

as mentioned earlier in this report [3]. Oxygen gas bubbles were also observed on the platinum counter electrode and this is expected during the deposition of WO_3 thin films as illustrated in the equation above as well. WO_3 thin films are characterized by a deep blue color which darkens as the film thickness increases. This color disappears when external bias is removed as illustrated in Figure 5.

![Figure 5](image)

**Figure 5:** (a) the deep blue films of WO_3 during deposition in Dr. Bob’s cell and (b) the disappearance of the blue color when the voltage is switched off while the electrode is in solution.
Figure 6: Eighty cycles of cyclic voltammetry sweep for WO$_3$ films on ITO in 0.5 M sodium chloride solution

As a way of testing the stability of the thin films, 80 consecutive cycles of cyclic voltammetry were run in a NaCl medium. The films did not show visible significant changes after this process (Figure 6). The voltammogram above also shows that the electrochemical performance of the thin films was not tainted. This dynamic might change with solar illumination but it is safe to say that the electrodeposited thin films were stable and could operate for a lot of cycles.
Figure 7: Cyclic voltammetry run for WO₃ films on ITO at varying scan rates in 0.5 M sodium chloride solution

Varying the scan rate caused a shift on the peak current and potential (Figure 7). In a slower voltage scan rate, the diffusion layer will grow much farther from the electrode resulting in a smaller flux to the electrode. Subsequently, the peak current is lower compared to that of faster voltage scan rates since peak current is proportional to flux towards the electrode.

Another interesting electrochemical behavior of the films was investigated using cyclic voltammetry. WO₃ thin films exhibit electrochromic properties in which they go through coloration during an intercalation process.
and decoloration during a deintercalation as shown in the Figures 8 and 9 respectively. The experiment was carried out using the Gamry potentiostat as before with the standard three electrode system using platinum (Pt) as the counter electrode and Ag/AgCl as the reference electrode. The electrolyte was a 1 M solution of Nitric acid (HNO$_3$). The applied potential was varied between $+0.6$ V and $-0.6$ V and back to $+0.6$ V at a scan rate of 50 mV/s. A blue coloration of the thin films on ITO substrate was observed during the first half of the cyclic voltammetry sweep in which nitric acid supplies a proton (H$^+$) according to the reaction below:

$$H_xWO_3(colored) \rightarrow WO_3(bleached) + xH^+ + xe^-$$  \hspace{1cm} (6)

**Figure 8:** The observed color changes during a proton intercalation (coloration)
Figure 9: The observed color changes during de-intercalation (bleaching)

The supplied proton gets inserted into the layered structure of the WO$_3$ thin films resulting in a deep blue color. When the bias was reversed, the films got bleached because the protons were repelled out of the structure of WO$_3$. The intensity of the color during intercalation is directly proportional to the surface area available for the H$^+$ ions to intercalate with the WO$_3$ film [3]. A diffusion coefficient during intercalation and de-intercalation for the WO$_3$ film was calculated using the Randles-Servick equation as reported in [10]:

$$D^{1/2} = \frac{ip}{2.72 \times 10^5 \times n^{3/2} \times C_0 \times V^{1/2}}$$  \hspace{1cm} (7)

where $ip$ is the cathodic peak current due to proton intercalation, $n$ is the number of electrons transferred (assumed to be 1), $C_0$ is the concentration
in bulk and $V$ is the scan rate. The diffusion coefficients for intercalation and deintercalation were calculated to be $7.43 \times 10^{-13}$ and $5.4 \times 10^{-17}$ cm$^2$/s, respectively.
Electrodeposition of ZnTe occurs in two steps, the underpotential reduction of tellurium dioxide and the cathodic deposition of zinc ions. The cyclic voltammogram of ZnTe in Figure 10 shows a cathodic (reduction) peak around -0.3 V. This corresponds to the reduction of HTeO$_2^-$ to Te and water according to the following equation:
$HTeO_2^+ (aq) + 3H^+ (aq) + 4e^- \rightarrow 2H_2O(aq) + Te(s)$  \hspace{1cm} (4)

The second cathodic peak is observed at -0.8V, corresponding to the under potential reduction of Zn to form ZnTe as shown below [23, 24]:

$$Zn^{2+}(aq) + Te(s) + 2e^- \rightarrow ZnTe(s)$$ \hspace{1cm} (5)

It is important to note that the deposition stock solution had a large Zn:Te ratio of $3 \times 10^3$ which was reported by T Mahalingam, et al [21]. Tellurium is less electropositive than zinc hence it would naturally deposit as a metal. Increasing zinc in solution encouraged the deposition of zinc due to its abundance in solution and reduced competition from tellurium. Also, an increase in tellurium by adding tellurium dioxide would reduce its solubility. Deposition at more negative potentials (-1.2 V) resulted in hydrogen evolution and this phenomenon was reported by other researchers as well. Lower pH values, (2.2) resulted in the deposition of thick, grey zinc flakes which barely adhered to the substrate and fell off in solution.
Figure 11: A steady current output during chronoamperometric deposition of ZnTe thin films onto ITO glass substrate in 0.15 M ZnSO₄, 0.5 mM TeO₂ and 0.12 M H₂SO₄ at 98 °C.
Figure 12: Cyclic voltammetry sweep on a composite WO$_3$/ZnTe film on ITO in 0.5 M NaCl solution at 25 °C

Figure 11 shows the steady current during the deposition of ZnTe thin films on top of WO$_3$ thin films. It is interesting to note that when the potentiostat settings were such that a negative current represented reduction, the voltammogram of the composite WO$_3$/ZnTe electrode in Figure 12 had the shape of the WO$_3$ thin films with reduction peaks for ZnTe deposition. This suggests that there might be some spaces where the WO$_3$ thin films are slightly exposed and not completely covered by the ZnTe layer.
Figure 13: SEM imaging for a) WO$_3$ thin films on ITO and b) ZnTe thin films on ITO

Figure 14: EDS Analysis of a) WO$_3$ thin films on ITO and b) ZnTe thin films on ITO
Surface morphology was examined using a JEOL JSM 4600 SEM functioning at 5 kV. The WO<sub>3</sub> thin films showed an amorphous structure with uniformly distributed particles and a few conglomerates (Figure 13). These films had a dense framework with a good adherence to the ITO glass substrate. The ZnTe thin films which are characterized by a reddish-brown color also uniformly covered the surface and adhered well to the substrate. The thin films seem to consist of spherical clusters building up around a nucleus. EDS analysis (Figure 14) showed the presence of all the elements that had been deposited in their correct atomic percentages (Table 3). S.A Mohamad, et al [26] indicated that the deposition temperature had a direct effect on the Zn:Te ratio deposited. This ratio increased with a decrease in temperature meaning more Zn was deposited compared to Te. This is

<table>
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<th>At%</th>
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because the dissolution of Te is favored by high temperature hence as the temperature decreases less and less is deposited from solution.

**Figure 15**: LSV sweep for water splitting using WO\textsubscript{3} electrode and WO\textsubscript{3} sensitized with ZnTe under 1 kW/m\textsuperscript{2} (1 sun) illumination

The water splitting capability of the composite electrode was investigated by linear sweep voltammetry (LSV). Figure 15 above shows a comparison of the performances between a WO\textsubscript{3} electrode and a composite WO\textsubscript{3}/ZnTe. The black arrow shows the reduction in voltage between the two electrodes in favor of the composite electrode. The reduction in voltage affirms the suggested hypothesis. It is evident that sensitization increases charge separation and white light utilization resulting in a reduction in the
voltage required to initiate water splitting. Upon illumination p-ZnTe, which has an excess of holes will have the electrons excited and transferred to p-WO$_3$ with an excess of electron holes thereby improving the water splitting efficiency. As for the WO$_3$/p-ZnTe composite films, the charge-transfer process could be explained by the p-n photochemical diode since deposited WO$_3$ and ZnTe are n-type and p-type respectively. The charge transfer process between the thin films can could be explained by a p-n photochemical diode concept. Upon solar illumination, the excess of electrons in valence band of WO$_3$ are excited into its conduction band as shown in Figure 16. The majority of electrons in the WO$_3$ conduction band and holes in the p-ZnTe valence band recombine by charge transfer through the interfaces between the two semiconductors. These electrons can be further excited into the conduction band of ZnTe increasing the separation of these charges from their holes in the valence band of WO$_3$. The recombination of the photogenerated charges in the respective semiconductors is suppressed. Thus, the photogenerated electrons with strong reduction power will accumulate in the conduction band (ZnTe) as well as leave the relative photogenerated holes with strong oxidation power in the valence band (WO$_3$). This improved charge separation results in availability of more charge-hole pairs with enough energy to split water and this consequently cuts the overvoltage and cost encountered in water splitting.
Figure 16: Charge-transfer process in n-WO₃/p-ZnTe composite film

If n-ZnTe films were to be used together with n-WO₃ as shown in Figure 17 below, there would be more recombination of electron hole pairs within the respective semiconductors. This is because electrons would be excited from the valence to conduction band of WO₃ and since there are no excess holes in the valence band of ZnTe for these electrons to recombine with, they would recombine within WO₃ itself. Poor charge separation leads to an increased overvoltage.
Figure 17: Charge-transfer process in WO$_3$/n-ZnTe composite film

\[ 2H^+ + 2e^- \rightarrow H_2 \text{ (Cathode)} \]

\[ \text{Anode: } H_2O + 2h_{VB} \rightarrow \frac{1}{2}O_2 + 2H^+ \]

Figure 18: EIS showing Nyquist plot of a) WO$_3$ thin films at low potential and b) WO$_3$/ZnTe composite on ITO substrate at a higher potential under 1 sun illumination.
Electrochemical impedance spectroscopy (EIS) was performed on both the WO$_3$ and the WO$_3$/ZnTe composite electrodes. On a Nyquist plot, the electrochemical impedance is proportional to the radius of the semicircle. Figure 18 and equivalent circuits in Figure 19 show that the composite electrode had lower impedance which consequently shows that there was an improved charge transfer and separation. The heterojunction formed by annexing the n-WO$_3$ and p-ZnTe provides a better charge transport pathway which allows for better utilization of solar energy.
WO$_3$ thin films and ZnTe thin films were successfully synthesized using electrodeposition. From the results, it is evident that sensitizing WO$_3$ using ZnTe reduces the potential at which water splitting is achieved. This is because there is improved charge transfer and separation between the two semiconductors. However, this concept should be used on a different substrate due to the limitations of using ITO glass. Adding a protective carbon layer would have increased the durability of the electrode in solution; however, the carbonization step which involved heating the electrode at 500 °C for 4 hours had negative effects on the conductivity of ITO glass. The conductivity of the glass significantly reduces after exposure to high temperatures. This negatively affects the overall efficiency of the electrode in water splitting. Some improvements can be made in the future by using a different substrate like platinum foil.
References


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