Electrosynthesis of TiO$_2$-Au Composites for Water Splitting Applications and Their Photoelectrochemical Characterization

A thesis presented

By

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To

The Department of Chemical Engineering

In partial fulfillment of the requirements
For the degree of

Master of Science

In the field of

Chemical Engineering

Northeastern University
Boston, Massachusetts

(08, 11, 2008)
A mon appui,
A mon rêve interdit!
A mon papillon
ACKNOWLEDGEMENT

First of all, I gratefully acknowledge Professor Elizabeth J. Podlaha for giving me the opportunity to work with her. I appreciate in particular her patience and tolerance. It has been an unforgettable experience, for Professor Podlaha has been a great mentor to me.

I would also like to thank my committee members, Dr. Sacco and Dr. Kurtz, for investing their time to read and provide feedback on my thesis.

Special thanks to the following individuals:

- Mariam Ismail, for her help with SEM, XRD and for being the great friend that she is.
- Edward Viveiros for his help and input.
- Stephanie Fernandez for being my smoking buddy.
- Rosa Daneshvar and Ha Na Kim, my labmates, for hogging the lab equipments.
- Dr. Julius Warzywoda, for his help with SEM and XRD analysis.

Finally, I would like to thank my family for their support throughout this process. Their encouragements and faith in me kept me going throughout it all.
ABSTRACT

Hydrogen is one alternative clean fuel for micro-scale devices when generated by solar irradiation through water splitting. The photoelectrolysis of water has been intensively studied since the seminal work of Fujishima and Honda in 1972 where titania was used as an anode photocatalyst [1]. While TiO$_2$ is an attractive material because it is inexpensive and a well known catalyst for water dissociation, one of the major drawbacks that limits its practicality is that it only absorbs light in the UV region. Recent results of combining Au nanoparticles with TiO$_2$ has been suggested to prevent electron hole recombination of the photoexcited titania hence enhancing its photoelectrochemical performance [2-3].

In this study, three layers of TiO$_2$ is electrosynthesized on ITO substrates using the generation of base method followed by annealing steps in between each deposited layer and a final heat treatment to ensure the anatase crystallinity of the deposits. [4]. The thickness of the films was between 2-3 µm with a cracked morphology. Au nanoparticles were subsequently electrodeposited onto the electrogenerated TiO$_2$ and pulsing conditions that affect the Au nanoparticle size and uniformity were investigated. Pulsed waveforms included a nucleation, growth and dissolution step. Results indicate that the first nucleation step is key in determining the size of the particles and the clumps formed as well as their density.

Photoelectrochemical tests including step photoresponse analysis under different light sources, electrochemical impedance analysis and intensity modulated photocurrent spectroscopy techniques were employed to characterize the enhanced photoelectrochemical response of three different forms of the TiO$_2$-Au composite: (1) TiO$_2$ decorated with Au nanoparticles, TiO$_2$/Au, (2) TiO$_2$ with embedded Au
nanoparticles in a sandwich fashion, TiO$_2$/Au/TiO$_2$, and (3) TiO$_2$ with embedded and
decorated Au nanoparticles, TiO$_2$/Au/TiO$_2$/Au. Results indicated that electrodeposited
gold on titania resulted in the highest photocurrent response under UV irradiation (25 µA,
14 µA/cm$^2$) and a red-shifting of the photoresponse of the composite. The second best
photoresponse was obtained with the TiO$_2$/Au/TiO$_2$/Au samples (17 µA, 9 µA/cm$^2$), and
the third best response compared to pristine titania was generated with the TiO$_2$/Au/TiO$_2$
sandwiched samples (11 µA, 6 µA/cm$^2$). Aging of the samples and additional
photoelectrochemical tests resulted in a decreased in the photocurrent response.

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1.0 INTRODUCTION

Hydrogen is one alternative clean fuel for micro-scale devices when generated by solar irradiation through water splitting. The thermodynamic potential required for splitting water into hydrogen and oxygen at ambient conditions is 1.23 V, which represents a minimum energy requirement. When accounting for energy losses to drive the reduction and oxidation half reactions, an overall voltage of 1.6-1.8 V is needed to decompose water, where most of these losses are attributed to the sluggish kinetics of O₂ evolution [1]. Due to the latter effect, most of the attention has been directed towards improving the design of a photoanode where oxygen evolution occurs [2,3,4,5,6]. The photoelectrolysis of water has been intensively studied since the seminal work of Fujishima and Honda in 1972 where titania was used as an anode photocatalyst [7]. While TiO₂ is an attractive material because it is inexpensive and a well known catalyst for water dissociation, one of the major drawbacks that limits its practicality is that it has a high band gap of 3 eV, which absorbs photons in the UV range, utilizing only 5% of solar radiation at most. In order to induce a better charge separation within a semiconductor film, a wide variety of approaches have been considered. One such approach is to sequentially couple different types of semiconductor materials where it becomes possible to promote charge separation by accumulating charge carriers (e⁻, h⁺) in two or more semiconductor layers [8]. O’Reagan and Grätzel [2] developed a dye-sensitized solar cell, where the electrolyte continuously oxidizes and reduces the dye molecules leaving behind no net change and a dye absorbing light in the visible region resulting in a photoexcited electron being rapidly injected into the conduction band of TiO₂. Another approach involves the deposition of noble metal nanoclusters [9,10] in order to maximize...
the efficiency of photocatalytic water splitting reactions. The role of the noble metal is to store photogenerated electrons and prevent them from recombining with holes in order to promote interfacial charge transfer within these composites. Figure 1 represents a schematic of the charge separation in a TiO$_2$/Au composite [11].

![Figure 1: Charge separation in a TiO$_2$/Au composite [11]](image)

When a metal comes into contact with a semiconductor, the electrochemical potential should equilibrate through the system. If, before contact, the metal and the semiconductor have different potentials, then when contact is made, charge will flow to the material with the smaller potential until equilibrium is reached. This phenomena is generally dictated by the work function ($\Phi$) which is defined as the average work needed to move an electron from the solid to the surface [12]. If $\Phi_{\text{metal}} > \Phi_{\text{semiconductor}}$ the electrons are transferred from the semiconductor to the metal, leaving behind a depletion region in the semiconductor characterized by the bending of the conduction and the valence bands [13]. Figure 2 illustrates a schematic of a Mott-Schottky plot in the case
where $\Phi$ of the metal is greater than $\Phi$ of the semiconductor which is the case of TiO$_2$ an n-type semiconductor and gold nanoparticles [14].

![Energy diagram of a metal and a n-type semiconductor](image)

Figure 2: Energy diagram of a metal and a n-type semiconductor, with $\Phi_{\text{metal}} > \Phi_{\text{semiconductor}}$: a) before contact and b) after contact [14]

It has been reported that the deposition technique plays a crucial role in determining the activity of the semiconductor-metal composite [15]. Electrodeposition is the technique used in this work because it allows the deposition of a wide variety of metals, it is a cheap method to synthesis thin films as well as it provides the ability to deposit into deep recesses and onto irregular geometries.
In this particular work, electrosynthesis of titanium dioxide films as well as the electrodeposition of gold nanoparticles/clusters have been investigated towards the photocatalytic activity of water dissociation. Our approach is to localize photoabsorption as well as bandbending within a few nanometers of the titania surface by incorporation of gold nanoparticles on the surface of the titanium dioxide and buried gold nanoclusters within the semiconductor matrix. The existence of these noble metal clusters within the dielectric titania matrix is expected to cause a redshift in the photoelectrochemical response, making use of the visible spectrum [16]. Furthermore, the incorporation of the gold nanoparticles induces defects and changes within the oxide, giving rise to a higher level of photo-excitation [17]. Electrochemical, photoelectrochemical as well as Intensity Modulated Photocurrent Spectroscopy (IMPS) techniques were employed in order to characterize the deposits and inspect the efficiency of the transport and reaction kinetics of the photo-generated electrons and holes as well as compare the photo-activity of the TiO₂/Au composite versus bare titanium dioxide. The following steps have been performed throughout this study:

1) Titanium dioxide photoanodes have been electrosynthesized via a localized and indirect precipitation technique driven by an applied external potential. The deposit consisted of a hydrous titanium oxo-hydrides gel which was then heated in order to obtain crystalline anatase titania. This approach follows that of Georgieva et al. [18] who electrosynthesized anatase TiO₂ on stainless steel. In this thesis similar conditions are used to deposit TiO₂ on indium tin oxide, an optically transparent conductive material that can be directly used in the development of a solar cell.
2) Pulsed galvanostatic (constant current) gold electrodeposition was employed and different waveforms were examined which resulted in various particle shapes and densities. It is the first comprehensive study of a using different pulse, growth and dissolution steps to help shape the nanoparticles on the electrosynthesized TiO₂ surface.

3) Photoelectrochemical testing was performed on TiO₂ and TiO₂/Au photoanodes in a basic medium and current transient plots were generated as well as impedance and dynamic transfer function spectra were constructed. These experiments relate the electrosynthesis and electrodeposition conditions with the photoelectrochemical property necessary for water splitting.

The electrochemical techniques investigated provide a niche in deposition: the process can be used to deposit material onto irregularly shaped and recessed substrates. Thus, the results of this work present conditions to develop solar cells on irregularly shaped substrates and open up the potential to create micro-size devices.
2.0 LITERATURE REVIEW

2.1 Photoelectrolysis

After the seminal publication of Fujishima and Honda of 1972 [7], the possibility of clean hydrogen fuel at low cost became the aim of much scientific work. Nozik [19] studied the effect of the intensity of ultra violet radiation on titania rutile electrodes. Hardee and Bard [20] prepared a n-type Fe₂O₃ photoanode and tested its behavior in different pH solutions as well as with different light intensities. Mavroides et al. [21] confirmed the possibility of water decomposition on SrTiO₃ anodes with an improved quantum efficiency at zero bias voltage. The overall efficiency of these photoanodes was very small and hopes of finding means to photosplit water began to fade. Later on, in the 1980s, more efficient photoanodes were engineered, on the other hand, the cost of the semiconductor materials were high enough to drive sponsors away from funding this research area [22].

A minimum energy requirement of 1.23 V is needed to split water, but due to the added kinetic, ohmic and mass transport resistances, a value of 1.8 V is necessary to achieve a reasonable rate. In a semiconductor electrode, the maximum energy attainable is the band gap energy. However the band gap energy is only obtainable at zero photocurrent, since a growth in the photocurrent leads to a decrease in the available potential. Usage of a high energy gap material would be of great interest. On the other hand, these semiconductors would not respond to light excitations in the visible region, making them only responsive to a fraction of the solar spectrum [22].

Titania has been thoroughly investigated because of the wide range of its application, low cost and non-toxicity. Some of these applications include the
degradation of pollutants and organic molecules [23,24], and its implementation in gas sensors because of its change in conductivity upon gas adsorption [25]. Most importantly, titanium dioxide is being extensively studied for the photoelectrolysis process, where a water molecule splits into its constituents to generate H₂ and O₂. Furthermore, TiO₂ also possesses strong oxidizing ability, high stability and resistance to corrosion in aqueous media [26].

When a semiconductor photoanode is bombarded by photons in an aqueous media, hydrogen starts evolving at the cathode and oxygen at the anode. The water splitting reaction can be written as follows [21]

\[
\text{TiO}_2 + h\nu \rightarrow \text{TiO}_2(e^-, h^+) \quad (1)
\]
\[
2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- \quad (2)
\]
\[
\text{H}_2\text{O} + 2h^+ \rightarrow \frac{1}{2}\text{O}_2 + 2H^+ \quad (3)
\]

In a basic medium, the mechanism that has been postulated is that hydroxyl radicals are the ones that capture the generated holes and not water [27]

Reaction mechanism at a TiO₂ anode

\[
h^+(\text{TiO}_2) + \text{OH}^- \rightarrow \text{TiO}_2 + \text{OH} \quad (4)
\]
\[
\text{OH} \rightarrow \text{O}^-_{(aq)} + \text{H}^+_{(aq)} \quad (5)
\]
\[
h^+(\text{TiO}_2) + \text{O}^-_{(aq)} \rightarrow \text{TiO}_2 + \text{O}^*_{(adv)} \quad (6)
\]
\[
\text{O}^*_{(adv)} + \text{O}^*_{(adv)} \rightarrow \text{O}_2 \quad (7)
\]
Reaction mechanism at a Pt cathode

\[ e^{-}(TiO_{2}) \rightarrow e^{-}(Pt) \]  \hspace{1cm} (8)

\[ e^{-}(Pt) + H^+_{(aq)} \rightarrow H_{ads} \]  \hspace{1cm} (9)

\[ H_{(ads)} + H_{(ads)} \rightarrow H_{2} \]  \hspace{1cm} (10)

2.2 Brief Overview of Titanium Dioxide

2.2.1 Physical and Chemical Properties of TiO₂

Titanium dioxide, a naturally occurring oxide of titanium, exists in three different polymorphs: anatase, rutile and brookite. TiO₂ has been widely studied in the past few decades due to its remarkable electric, magnetic and catalytic activities [28]. TiO₂ as a photocatalyst has drawn much attention. The crystal structure data of the different polymorphs of titanium dioxide are summarized in Table 1 [28]. Figure 3 represents the crystal structures of the three different phases of TiO₂ [28].

<table>
<thead>
<tr>
<th></th>
<th>Rutile^a</th>
<th>Anatase^a</th>
<th>Brookite^b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal structure</td>
<td>tetragonal</td>
<td>tetragonal</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>Lattice constants (Å)</td>
<td>(a = 4.5936)</td>
<td>(a = 3.784)</td>
<td>(a = 9.184)</td>
</tr>
<tr>
<td></td>
<td>(c = 2.9587)</td>
<td>(c = 9.515)</td>
<td>(c = 5.145)</td>
</tr>
<tr>
<td>Space group</td>
<td>(P4_2/mnm)</td>
<td>(I4_1/amd)</td>
<td>(Pbc)</td>
</tr>
<tr>
<td>Molecule/cell</td>
<td>2</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>Volume/molecule (Å³)</td>
<td>31.2160</td>
<td>34.061</td>
<td>32.172</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>4.13</td>
<td>3.79</td>
<td>3.99</td>
</tr>
<tr>
<td>Ti—O bond length (Å)</td>
<td>1.949(4)</td>
<td>1.937(4)</td>
<td>1.87—2.04</td>
</tr>
<tr>
<td></td>
<td>1.980(2)</td>
<td>1.965(2)</td>
<td></td>
</tr>
<tr>
<td>O—Ti—O bond angle</td>
<td>81.2°</td>
<td>77.7°</td>
<td>77.0°—105°</td>
</tr>
<tr>
<td></td>
<td>90.0°</td>
<td>92.6°</td>
<td></td>
</tr>
</tbody>
</table>

Table 1: The crystal structure data of Titanium dioxide [28].
Rutile is the most extensively studied phase of titanium dioxide and contains six atoms per unit cell. Anatase contains twelve atoms per unit cell. In both phases, for a perfect crystal, every Ti atom is attached to six O atoms [28].

Since the flat-band potential of rutile is faintly more positive than that of the standard H$_2$ electrode, and the flat-band potential of anatase is more negative to it, the reduction of water molecules to hydrogen by photoexcited conduction band electrons takes place spontaneously on anatase polymorphs than on rutile. On the other hand, O$_2$ evolution occurs at similar rates on anatase and rutile since the potential of the photogenerated holes is above the potential of oxygen evolution. These two characteristics make anatase the only crystalline titania phase where photodissociation of
water molecules can take place without an external applied voltage [29]. In addition, the enhanced photoactivity of anatase over rutile is attributed to the larger bandgap of the former (3.2 eV versus 3.0 eV) which helps in increasing the surface redox potentials and prolonging the electron/hole lifetime [30]. Furthermore, Tang et al. reported that anatase thin film has a wider optical absorption edge than rutile resulting in a higher photoconductivity threshold energy [31]. The value of the absorption edge of anatase is equal to 387 nm and that for rutile is equal to 418 nm [32].

2.2.2 Photoelectrochemical Properties of Bare TiO₂

When subjected to irradiation (<350 nm), titania particles undergo charge excitation. The excited charges can either recombine or get transferred to the back of the electrode or to the surface where they get involved in chemical reactions. The photoelectrochemical screening depends on the light source, light intensity, the electrolyte used and the applied external bias [11]. Generally, at positive applied external bias, an increase in the photocurrent is observed since the photoanode acts as the positive electrode [4]. A colloidal TiO₂ suspension applied on optically transparent electrodes followed by heat treatment at 673K for 1 hour was prepared by Chandrasekharan and Kamat [11] with an area of 2.5 cm² and a 10 μm thickness. These bare TiO₂ films exhibited a around 0.1 mA photocurrent response upon UV irradiation with a 150 W Xenon lamp. The electrodes were maintained at +0.75 V versus SCE in a N₂ saturated 0.05 M NaOH solution. Lana-Villarreal and Gómez [4] reported a photocurrent value of around 0.1 mA upon irradiation of TiO₂ photoanode with UV light in a N₂ and O₂ saturated 0.05 M NaOH solution. The potential was maintained at -0.4 V versus Ag/AgCl/KCl saturated electrode. The illumination source was a 150 Xenon arc lamp
with an incident light intensity of around 1.1 W. The nanoporous thin film TiO$_2$ electrodes were prepared from an aqueous slurry of commercially available anatase nanoparticles. The slurry was spread on a 1.5 cm$^2$ F:SnO$_2$ transparent conductive glass plate. The thickness of the TiO$_2$ film was around 2.8 μm and was annealed in air at 450°C for 1 hour. Baeck et al. [33] used a thermally oxidized titanium foil at 400°C for 1 hour. This group reported a photocurrent density of around 0.78 mA/cm$^2$ for bare TiO$_2$ at zero bias versus Ag/AgCl in a 0.1 M sodium acetate electrolyte. The photoanode was irradiated with a 1 kW Xenon lamp. Georgieva et al. [18], electrosynthesized titanium dioxide films on stainless steel substrates. These hydrous deposits were then heated in air for 1 h at 400°C in order to obtain crystalline anatase films. The photoanodes were irradiated with a UVA lamp at a power density of 3 mW/cm$^2$ in a 0.1 M K$_2$SO$_4$ + 0.005 M oxalate solution at +0.5 V versus SCE. The maximum obtained photocurrent density value was around 0.1 mA/cm$^2$.

Multiple efforts have been undertaken by several research groups to extend the use of titania into the visible portion of the solar spectrum. Some of these approaches include doping the TiO$_2$ matrix with different elements such as nitrogen, cadmium [34], sulfur and carbon [35]. Other modifications include the preparation of titania nanotubes [36,37] dye-sensitized TiO$_2$ films [2,3]. Another approach employed to enhance the photocatalytic activity is to place metal nanoparticles on TiO$_2$ [4, 11, 38, 39, 40].
2.3 The Physical and Chemical Properties of Gold (Au)

2.3.1 Properties of Bulk Gold

The 5d level electrons in Au ($5d^{10} \, 6s^1$) are considered to be easily activated and become mobilised for the chemical reaction that is taking place. In addition, this latter effect explains the predominance of the Au$^{\text{III}}$ state. The electron in the 6s level tends to acquire an additional electron to complete its shell which leads to a higher electron affinity and accounts for the formation of Au$^{-1}$ state. Gold’s electrode potential, $E^o = +1.691 \, \text{V}$ is high for a metal indicating its resistance to corrosion and nobility in bulk properties. Gold crystals take the shape of a face-centered cube (fcc). There exists only one naturally occurring isotope of gold with a magnetic nucleus. Gold’s electrical resistivity is greater than that of silver and its optical absorption in the visible light region of the electromagnetic spectrum is due to the relativistic gap lowering of the 5d band and the Fermi level. The melting point of bulk gold is 1064.18 °C [41].

2.3.2 Properties of Gold Nanoparticles

As it has been indicated previously, bulk gold is an inert material, yet gold nanoparticles exhibit high catalytic activity especially towards the oxidation of carbon monoxide. Zhang reported that it is quite difficult to obtain highly dispersed gold particles, similar to those of palladium and platinum, mainly because of the melting point of gold. The melting point of Pt is 1769°C, that of Pd is 1550°C, both of which are considerably higher than that of gold (1063°C) [42,43]. What is interesting to note is that the melting point of gold nanoparticles with a diameter of roughly 2 nm is decreased to 300°C due to the quantum size effect [44].
In a face-centered cubic gold crystal, one would generally observe three low-index planes: (110), (100) and (111) where the latter plane has been viewed as the most stable one, having the lowest surface energy. Figure 4 [41] represents a schematic of the Au (100) (110) and (111) planes. Furthermore, the (111) plane of gold could be reconstructed under ultra high vaccum (UHV) conditions. The newly obtained structure has areas of both face-centered cubic and closed-packed hexagonal structures, where 23 atoms occupy positions that would be typically occupied by 22 atoms, thus rendering its surface energy even lower by squeezing in more atoms. The Au(110) plane also reconstructs under ultra high vacumm to form a highly stepped (111) surface [41].

Figure 4: Schematic of the gold (100) (left), (110) (middle) and (111) (right)

Finely dispersed gold nanoparticles exhibit high catalytic activity due to the fact that 60% of the atoms of a 2 nm diameter particle are located on the surface. These small particles are rich in energy because instead of using it in subdividing a bulky piece of gold, it is used in breaking the chemical bonds and this energy is then transferred to the free valances or dangling bonds that have been created. A decrease in the size of a particle leads to an increase in the number of atoms on the surface that are not bound to
their neighboring atoms. The unemployed or unused orbitals of these atoms generate a great effect on the physical properties of the particle, where the change in the physical property is often proportional to the inverse of the particle size. It has been noted that a decrease in the size of the particle leads to a diminishing in the overlapping of the bands of the valence electrons and are therefore replaced by distinct energy levels characteristic of an isolated atom. The latter effect which has been observed in Au$_{55}$ and smaller clusters results in the loss of the metallic activities like electrical conductivity and Mie plasmon resonnance. Furthermore, this phenomena is dependent on temperature, at elevated temperatures, metallic properties are observed, on the other hand, at low temperature, a non-metallic transition occurs [41].

The incorporation of noble metals on semiconductors for water splitting reaction has been extensively studied since it enhances the efficiency of the photocatalytic reaction and shifts the photo response towards the visible light region [9, 16, 45].

2.4 TiO$_2$/Metal Interactions

2.4.1 TiO$_2$/Au Composites

Preparation methods and techniques highly affect the size and shape of gold nanoparticles and their interaction with the support. For instance, the deposition-precipitaion of Au on TiO$_2$ results in hemispherical particles, while impregnation and photodeposition results in spherical ones. Moreover, calcination of the gold nanoparticles at temperatures greater than 200°C leads to an increase in the diameter of the nanoparticles [41].

Many studies have been conducted on the reduced surface of TiO$_2$ which consists
of either oxygen vacancies or hydrogen adsorption sites. In the former case, the number of oxygen atoms is less than that indicated by the metal-oxide formula, these surface defects act as nucleation sites for gold deposition [46]. Furthermore, it is believed that gold alters the band gap of titania. Electronic changes have been observed in the presence of gold nanoparticles near titanium ions where the Ti $2p$ level underwent a band-bending of 0.15 eV [41]. Utilizing argon ion bombardment of TiO$_2$(110) led to surface defects such as oxygen vacancies and Ti$^{3+}$ ions whereby deposition of gold on these defects led to a negative shift in the binding energy caused by a charge transfer from gold to the Ti$^{3+}$ ions. Oxygen vacancies are believed to be more present near gold nanoparticles in consequence of the Schottky junction at a metal-semiconductor interface. The charge transfer is possible with gold particles big enough to exhibit high electronegativity, but it is less likely with small particles [41]. The placement of the Au adatoms on the titania surface is crucial, for instance, above a five-fold surface Ti atoms of unrelaxed TiO$_2$(110), there was no metal-induced gap states [47]. On the other hand, placing a gold atom on top of a five-fold Ti atom after surface relaxation, led to a shift in the Au d-band closer to the Fermi-energy and metal-induced gap states were envisaged to be present [48]. An improved photochemical response in the UV region was reported when gold nanoparticles were deposited on nanostructured thin films of TiO$_2$ due to the hindering of electron-hole recombination rate and the presence of defect energy levels on the semiconductor surface [49].

The amount of gold loading plays a detrimental role in the photocurrent behavior of irradiated TiO$_2$/Au electrodes. Subramanian et al. [16] observed an increase in the photocurrent up to a 2% (wt. Au/wt. TiO$_2$) followed by a decrease at higher
concentrations. Such a decrease was seen due to the fact that an increase in the gold nanoparticle loading acts as a sink for the photogenerated electrons and could also block the active sites of titania. This group also suggested the following possible reactions occurring as a way to explain the photoelectrochemical processes involved in the TiO$_2$/Au composite [16],

\[
\begin{align*}
\text{Reaction} & \quad (1) \\
TiO_2(e^- + h^+) + OH^- & \rightarrow TiO_2(e^-) + OH^- \quad (11) \\
TiO_2(e^- + h^+) & \rightarrow TiO_2 \quad (12) \\
O_2 + e^- & \rightarrow O_2^- \quad (13)
\end{align*}
\]

The most important process responsible for a high current generation is electron-hole separation. Reaction (11) helps in enhancing the uncoupling of the charge carriers, since the OH$^-$ act as hole scavengers on the photoanode side, thus reducing the electron/hole recombination. One would expect that reaction (11) is improved in the presence of a metal, where electron accumulation occurs. On the other hand, the last two reactions (12,13) hinder the electron accumulation and transfer processes. In reaction (12) electron/hole recombination occurs and current efficiency decreases. Reaction (13) involves the scavenging of electrons by oxygen molecules, whereas gold acts as an electron sink, thereby shielding these generated electrons. Ultimately, the role of the gold nanoparticles is to allow for the generated holes to react at semiconductor/electrolyte interface, thereby increasing the amount of electrons accumulated within the semiconductor crystallites.

Upon contact between titania particles and gold nanoparticles, a negative shift of the Fermi level is observed indicating an increase in the electron accumulation within the
composite system. This electron accumulation causes the TiO\textsubscript{2}/Au junction to be more reductive than bare TiO\textsubscript{2}. Upon irradiation of the TiO\textsubscript{2}/Au photoanode, a charge transfer occurs from TiO\textsubscript{2} to Au nanoparticles until equilibrium is established between the composite system (Fermi level of Au = +0.45 V versus Normal Hydrogen Electrode). This negative shift in the Fermi level, making it closer to the conduction band of TiO\textsubscript{2}, is indicative of a better, more enhanced charge separation for the titania/gold system.

Furthermore, this group concluded that smaller gold nanoparticles cause a bigger shift in the Fermi level potential [39]. The gold nanoparticles act as an electron sink due to the double-layer charging around the metal nanoparticle. These nanoparticles exhibit quantized (single electron) charging [50].

Fine metal particles present in a dielectric such TiO\textsubscript{2} exhibit an enhancement in the electric field upon illumination of the semiconductor because of surface plasma resonance [51]. The surface plasmons are resonantly excited electromagnetic waves propagating along the metal/semiconductor interface and are greatly localized in its region [52]. An enhanced shift in the plasmon angles are observed upon coupling between the localized surface plasmon of the Au nanoparticles and the surface plasmon wave associated with the bulk dielectric [53]. For example, Zayats et al. [54] reported that a further shift in the plasmon angle is observed due to the covalant binding of cadmium sulfide (CdS) to Au nanoparticles due to the enhanced surface plasmon scattering and changes of the refractive index of CdS. Small spherical clusters of gold display a narrow absorption peak at 520 nm which is associated with the surface plasmon resonance of gold’s conduction electrons. Buso et al. [55] reported a red-shift in the TiO\textsubscript{2}/Au composite when gold nanoparticles were imbeded in the titania matrix. They
also concluded that a shift in the absorption peak to a value around 600 nm was only observed when the annealing temperature of the film exceeds 300°C and attributed this shift to the increase in the refractive index of the titania matrix. Furthermore, the particle morphology and concentration of Au nanoparticles did not affect the absorption spectra with samples annealed at the same temperature which contradicts observations made by other groups [39,40,50] who stressed the fact that the plasmon resonance wavelength is strongly dependent on the metal nanoparticle size, shape, loading and the dielectric property of the surrounding medium.

The mechanism involving the charge separation, accumulation and transfer within the TiO₂/Au composite has yet to be fully understood [40,56]. As of today, improvement of the phototoxicorecometrical response has been observed upon doping and deposition of a metal on a semiconductor [9,16,39,45]. Tian and Tatsuma [40] have verified that the photoexcited electrons at Au nanoparticles are capable of being injected into the TiO₂ matrix, hence an improvement of the incident photon to current conversion efficiency (IPCE) has been attained (~26%).

2.4.2 Other TiO₂ Modifications

Insertion of metals into the TiO₂ matrix as well as deposition of these metals onto the dielectric have been extensively studied. Researchers believe that these modifications could alter the energetics of the water splitting reaction by favoring an efficient charge transfer and minimizing the electron/hole recombination process [20]. For example, Wu et al. [38] studied the effects of transition metals such as palladium (Pd), chromium (Cr) and silver (Ag) on the photocatalytic performance of TiO₂. Metal loaded titania exhibited higher photocatalytic activities than pristine TiO₂ under visible light illumination.
Pd/TiO₂ showed the highest improvement in that particular study. Pingxiao et al. [34] studied the photocatalytic effect of nitrogen (N) and cadmium (Cd) doped TiO₂ particles. They demonstrated that the cadmium doping can facilitate the charge transfer and hinder the recombination of the photogenerated e⁻,h⁺ pairs. On the other hand nitrogen doping shifted the photoelectrochemical range of the composite to the visible light range.

Dambar and Klabunde [57] studied the effects of silver, carbon (C) and sulfur (S) doped TiO₂ films. Their studies proved that C, S, Ag⁺ - doped TiO₂ exhibited much improved photocatalytic activity towards the degradation of gaseous acetaldehyde versus pristine TiO₂ under UV and visible light irradiation. Ui et al. [58] studied the effects of silver and copper (Cu) particles on TiO₂ and found that the photoelectrochemical activity of the Ag/TiO₂ composite film was superior to the Cu/TiO₂ one. The difference in the activity was mainly attributed to the synergistic effect of the Ag/TiO₂ composite under UV radiation. Mentus [59] studied the electrochemical response of platinum (Pt)/TiO₂ composites and demonstrated a high catalytic activity towards oxygen reduction and bromide ion adsorption/oxidation. Jakob and Levanon [60] observed a enhanced photocatalytic activity with Au/TiO₂ and Ag/TiO₂ compared to Pt/TiO₂ composites. They attributed this enhancement to the fact that gold and silver retain the generated charge (e⁻), while Pt facilitates the charge transfer from the semiconductor to the electrolyte, resulting in a decrease in the photogenerated current. In the recent past years, sulfur doped titania has induced some interest with respect to its photocatalytic activity, for example, Ohno et al. [35] prepared a C⁴⁺ and S⁴⁺ doped TiO₂ and showed that this co-doped composite can exhibit a higher activity towards the oxidation of methylene blue and 2-methylpyridine under UV and visible light irradiation. Wang et al. [61] were
successful in preparing an efficient bismuth (Bi) and sulfur co-doped titania and demonstrated its highly efficient visible light photocatalytic properties towards the photodegradation of indigo carmine solution. Finally, Periyat et al. [62] studied the photocatalytic activity of sulfur doped titania towards the degradation of rhodamine dye under visible light irradiation and showed an improvement compared to pristine titania. All of these alterations were made to shift the band gap response of TiO$_2$ to higher wavelength radiations in order to tailor its response towards the visible light region of the solar spectrum.

2.5 Preparation of TiO$_2$ Electrodes

There exists different techniques concerning the preparation of titania semiconductor electrodes. For example, Wahl et al. [24] prepared three kinds of titanium dioxide electrodes. One way was via a sol-gel method, where the titania anatase deposits were formed on titanium rods by applying a solution of TiCl$_4$ and ethanol heating it in air at 450$^\circ$C. The rods were then dipped in a dichlorodiethoxytitanium solution and then dried at ambient temperature. Further annealing was performed at higher temperatures. Another preparation technique included the oxidation of titanium metal in oxygen at 600$^\circ$C for half an hour. The third technique included the formation of a microporous crystalline titania films by attaching the commercially available P25 (Degussa) powder to the titanium surface and then annealing at elevated temperatures. Sol-gel preparation of titania films is a widely used technique, for example Zhao et al. [63] where a solution of titanium isopropoxide and ethanol was used under vigorous stirring at low temperatures. Heat treatments were then performed to ensure the crystallinity of the titania films. Buso et al. [55] prepared a sol-gel derived titania film by mixing titanium butoxide,
acetylacetone and methanol. This solution resulted in a titania precursor which was then spin-coated on a silica glass and then annealed at 500°C. Paramasivam et al. [37] and Macak et al. [64] employed a different approach by creating TiO$_2$ nanotubes via an anodization process. The preparation technique briefly consisted of a titanium foil immersed in an acidic electrolyte, typically sulfuric acid and hydrofluoric acid where a high anodic potential was applied, leading to a formation of TiO$_2$ nanotubes. Heat treatment of the samples was then performed in order to increase the conductivity of the nanotubes.

The electrosynthesis technique has also been used to generate thin films of titania because of its low cost, simplicity and ease to control the film’s morphology [65]. Natarajan and Nogami [66] used a three-electrode setup, where Pt was used as a counter electrode and a SCE was used as a reference electrode. They deposited a Ti-precursor by dissolving the Ti powder in hydrogen peroxide and ammonia, then they removed the excess solvents by heating up the solution, thus obtaining a yellow gel. That yellow gel was then dissolved in 2 M sulfuric acid and 2 M nitric acid, to eventually obtain a red solution. This red solution was used as the deposition bath and its pH was adjusted to 1 and to 3. The deposition process on glass slides was carried out between -0.9 V to -1.4 V versus SCE. Lokhande et al. [65] carried out a cathodic galvanostatic deposition of TiO$_2$ films on glass substrates at room temperature. The solution bath consisted of 0.05 M TiCl$_3$ in concentrated hydrochloric acid in 1:2 ratio. Ethylene-diamine-tetra acetic acid was added under constant mixing. A solution of ammonium hydroxide was added. The solution formed a whitish precipitate at a pH equal to 12.2. The deposition process was carried out in a three-electrode cell, a platinum mesh acted as the counter electrode, and a
glass substrate was used as the working electrode. Galvanostatic deposition was carried out at constant currents between 0.5-25 mA/cm² for 30 minutes. Karuppuchamy et al. [67] carried out the electrosynthesis of titania films on glass substrates at -1.2V versus SCE. The bath consisted of 0.02 M TiOSO₄, 0.03 M H₂O₂ and 0.1 M KNO₃. The pH of the solution was maintained at 1.8 and the deposition process was carried out at 10°C, leading to the formation of a TiO(OH)₂ₓH₂O gel on the glass substrate. Georgieva et al. [18] used a similar solution bath as Karuppuchamy et al. [67], on the other hand they were able to perform the electrosynthesis process at room temperature. Briefly, the aqueous solution consisted of 0.02 M TiOSO₄, 0.03 M H₂O₂, 0.05 M HNO₃ and 0.1 M KNO₃. The resulting pH was equal to 1.4, which made the deposition of the TiO₂ precursor possible at room temperature. The cathodic electrosynthesis was performed in a three-electrode cell. Stainless steel 304 substrate was used as the working electrode, a platinum plate was used as the counter electrode and a mercury sulfate Hg/Hg₂SO₄/H₂SO₄ (MSE) was used as the counter electrode. A value of -2.0 V versus MSE for 1 hour was chosen to insure good adhesion and thickness. Multilayers were electrosynthesised by performing heating steps between successive layers. In all the above mentioned examples, heating the samples at elevated temperature was done in order to obtain crystalline films.

2.6 Methods of Preparation of Gold Nanoparticles

Methods of preparation of the semiconductor-metal catalyst play an important role in the photochemical activity of the overall system. The size of the gold nanoparticles is key in obtaining active catalysts for several reactions. In most cases, such as carbon monoxide oxidation, only small gold nanoparticles (< 5 nm) exhibit high
catalytic activity [43]. Most gold precursors used in preparing supported gold catalysts are salt complexes where the oxidation state of gold is typically +3 since the latter is more stable than the +1 oxidation state. Moreover, the size of the gold nanoparticles highly depend on the gold ion concentration, the pH and the temperature of the solution used. The $\text{Au}^{3+}$ atoms are easily reduced by performing thermal treatment since gold oxides are typically unstable in air [41].

2.6.1 Gold Impregnation Using Chloride Precursors

Impregnation was one of the first methods used to prepare supported gold catalysts due to its simplicity. The most often used precursors were chloroauric acid or $\text{HAuCl}_4$ and gold chloride or $\text{AuCl}_3$. After thermal treatment in air, the size of the gold nanoparticles increased to 10-35 nm which led to poor catalytic activities [41]. The emergence of these large gold particles is due in part to the presence of the chloride ions which promote mobility and agglomeration of gold nanoparticles during thermal treatment. The chloride ions are believed to poison the catalyst and remain present even after calcination to 873 K, on the other hand, reduction with hydrogen removes it as HCl. An increase in size was observed for thermal treatment in $\text{H}_2$ and in air, on the other hand, the size of the gold nanoparticles treated in $\text{H}_2$ was smaller than in air [68]. It has also been observed that some of the $\text{AuCl}^-$ ions interact with $\text{TiO}_2$ during impregnation at a pH <1 which leads to a much smaller particle size roughly around 3 nm versus an unwashed sample where the mean particle size is around 10 nm [69]. The method of impregnation is not a realistic method for obtaining well-dispersed gold nanoparticles, because of the need to recover and re-use the gold lost in the washing process [41].
2.6.2 Gold Coprecipitation Using Chloride Precursors

Coprecipitation was first utilized in obtaining gold nanoparticles in 1987 [70]. It was done by adding sodium carbonate to an aqueous solution of HAuCl₄ and the nitrate of the metal which leads to the production of the support. After which the coprecipitates were washed and thermally treated in air. This method led to high gold dispersion with particles having a diameter less than 10 nm, and to oxide surface areas larger than the ones obtained in the absence of gold. In addition, some of the formed gold nanoparticles could be embeded in the support’s lattice. It is not clear in employing this method whether all the gold present in the solution is precipitated. Moreover, the nature of the precipitate is not clearly understood. This method works for certain metal oxides, because the rates of precipitation of the two precursors and their attraction is key in determining the size of the gold nanoparticles [41].

2.6.3 Deposition-Precipitation Employing Chloride Precursors

Deposition-precipitation is a method where metal hydroxide is supposed to precipitate on the oxide support as a result of gradually raising the pH of the solution. This procedure was originally developed by Geus and colleagues [71]. The method has various variations, such as the pH of the solution, the temperatures of the precipitation and washing, and the use of multiple bases. A typical preparation technique is as follows: after immersing the support in an aqueous HAuCl₄ solution, the pH of the solution is adjusted to 7 or 8 by adding sodium hydroxide or sodium carbonate, then, the sample is heated to roughly 342 or 353 K while stirring for a hour. Afterwards, thorough washing with water at roughly 323 K is applied to the as prepared sample in order to get rid of the sodium and the chlorine salts. The final product is then dried under vaccum at
373 K and usually thermally treated in air at much higher temperatures. The deposition-precipitation method works well with oxide supports having a point of zero charge or PZC greater than 5, these supports include titania, typically P25 Degussa, alumina, ceria and zirconia as well as zeolites. It has also been observed that the gold particles’ size decreases with increasing pH [41].

2.6.4 Deposition-Precipitation Utilizing Urea

Urea or CO(NH₂)₂ acts as a ‘delay-base’ since at room temperature and when it is dissolved in the support’s suspension in the aqueous metal salt solution, there is no chemical reaction. Hydrolysis occurs when this mixture is heated above 333 K. At first, HAuCl₄ is added to a suspension of the support in a urea solution having a temperature of 353 K. The deposition-precipitation was carried out for at least four hours in order to obtain small gold nanoparticles with a mean diameter of 3 nm. It was found that most of the gold in the solution was deposited onto the support. After four hours the pH rose from roughly 3 to 7 and hit a plateau. After that, the samples were washed with water, then dried at 300 or 363 K under vaccum. The last step involved calcination in air at 573 K. Moreover, the decrease in the deposition-precipitation time led to a decrease in the size of the gold nanoparticles [41,69]. Table 2 summarizes the effect of the deposition time on the mean diameter of gold nanoparticles deposited onto titania [41].
Table 2: Au/TiO₂ samples prepared by deposition-precipitation with urea at 353 K with a gold loading of 8 wt.%. [41]

<table>
<thead>
<tr>
<th>Oxide support</th>
<th>BET surface (m² g⁻¹)</th>
<th>PZC</th>
<th>DP time (h)</th>
<th>Final pH</th>
<th>[Au] (wt.%)</th>
<th>[Cl] (wt.%)</th>
<th>( \bar{d}_{\text{Au}} ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>45</td>
<td>~6</td>
<td>1</td>
<td>3.0</td>
<td>7.8</td>
<td>0.041</td>
<td>5.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>6.3</td>
<td>6.5</td>
<td>0.122</td>
<td>5.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4</td>
<td>7.0</td>
<td>7.7</td>
<td>&lt;0.03</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>16</td>
<td>7.3</td>
<td>6.8</td>
<td>&lt;0.03</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>90</td>
<td>7.8</td>
<td>7.4</td>
<td>&lt;0.03</td>
<td>2.4</td>
</tr>
</tbody>
</table>

The difference with the deposition-precipitation method with urea and the one without urea is that the former leads to small nanoparticles but with a longer precipitation time. On the other hand, unlike the typical deposition-precipitation, all the gold in solution is deposited onto the support. Therefore, it will be easier to prepare samples with the same gold loading and with different particles sizes by controlling the time of precipitation [41].

2.6.5 Anion Adsorption

In order for anion adsorption to occur the pH of the typically aqueous HAuCl₄ solution needs to be lower than the point of zero charge of the oxide support which makes the surface’s support positively charged. This method was employed to synthesize Au/TiO₂ at a fixed pH of 2. It was carried under various time and temperature conditions either 293 or 353 K. It was found that the gold loading never exceeded 20% of the gold in the solution which corresponds to 1.5 wt% of gold loading onto the support. The mean average of gold nanoparticles was between 4 and 6 nm. The ions present in the solution at the above specified temperatures are AuCl₃(OH)⁻ and AuCl₄⁻. These ions have a point
of zero charge roughly equivalent to 6 and can form electrostatic interactions with titania [41].

2.6.6 Preparation Methods Using Chloride-Free Gold Precursors

2.6.6.1 Deposition of Gold-Phosphine Precursors

Since chloride ions poison the catalyst, preparation methods that do not involve chloride precursors are highly desirable. Gold phosphine complexes such as [AuI(PPh3)]NO3 and [Au3Au60(PPh3)8](NO3)3 have been employed for the preparation of supported gold catalysts. The oxide supports were impregnated with a solution of the gold-phosphine precursor in dichloromethane followed by evaporation of the solvent. Gold particles with 16 nm average diameter were obtained [41].

2.6.6.2 Chemical Vapour Deposition (CVD)

In the case of chemical vapour deposition, a gaseous organogold compound reacts with the surface of the support, onto which it reduces to particles of gold, or to a thin film if the surface is flat. Dimethylgold acetylacetonate is the only suitable compound for this procedure. The process is carried out at 306 K, which gave after calcination small nanoparticles on titania with an average size of 4 nm. On the other hand, the size distribution varies greatly, unlike in deposition-precipitation. The advantage of this method is that a chloride-free gold precursor can be used and the adsorption of gold nanoparticles can be achieved over virtually any support. On the other hand, the preparation must be conducted in the absence of air and moisture [41].

2.6.6.3 Cation Exchange

So far, the only cation that has been used to prepare gold catalysts by exchange with zeolites or cation adsorption on oxide supports is AuIII [72]. Cation exchange acts as
an efficient way of introducing highly dispersed metal particles into zeolites. This method has also been used for depositing gold onto oxide supports by cation adsorption, where the point of zero charge of the support has to be lower than the pH of the solution in order to make the oxide surface negatively charged. Furthermore, the deposition technique needs to be performed at room temperature in order to prevent the cation decomposition. Gold and titania catalysts were successfully made at 298 K with a solution pH of 9 which yielded gold nanoparticles with an average diameter of 2.5 nm after calcination at 573 K. On the other hand, the gold content was very low, about 1 wt % [73].

2.6.6.4 Colloidal Gold

The method of preparing supported gold catalysts by colloidal gold involves dipping the support in the colloidal suspension followed by washing and drying. Au/TiO\textsubscript{2} samples have been prepared by depositing colloidal gold in diisopropylether, followed by calcination at 573 K. On the other hand sintering the small gold nanoparticles that have an average size of 5 nm was observed. Typically, the size of the particles deposited should not be significantly larger than the ones already existing in the colloid. The advantage of using this method is that the size of the particles is controllable, the size distribution of the nanoparticles is narrow and the gold particles are already reduced [41].

2.6.7 Sol-Gel Preparation Technique

Sol-gel involves the hydrolysis of a metal alkoxide in a water-alcohol solution of H\textsubscript{AuCl\textsubscript{4}}. After which, the gold is reduced either thermally or by UV radiation. Usually, the gold particles obtained are large for the use for carbon monoxide oxidation, with an
average diameter of 20 nm. In order to obtain smaller gold nanoparticles, the sol-gel process was performed in the presence of gold colloids with a particle size of roughly 2 nm. To avoid agglomeration, alkanethiolate was used with the colloids. Afterwards, a calcination step was performed at 700 K to remove the ligand and crystallize the TiO₂ support. The final gold particle size was around 6 nm, with a 6 wt % loading. This method is not suitable for preparing small gold nanoparticles for the case of carbon monoxide oxidation. Furthermore, the gold particles seem to be embedded in the support and therefore unreachable for the reactants to undergo transformation [41].

2.6.8 Atom Beam Deposition

One method consists of the vaporisation of metal atoms from a rod with a laser beam to create a plasma. An inert gas is introduced into the vacuum chamber which induces cluster nucleation and growth. At the end, clusters of well controlled size around 2-3 nm are obtained on alumina, zirconia and titania. Only reduced clusters are adsorbed onto the surface. The disadvantage of this method is that the gold loading is usually low, around 0.1 wt %, independent of the duration of the vaporisation. This method is ideal in studying the support/nanoparticles interaction since the particle size is almost identical. The other method consists of sputtering of a highly pure gold target with argon ions. These sputtered atoms are then deposited onto the surface of the support. This method yields larger gold loading than the former one, typically around 1.4 wt % for a 195 minute sputtering duration. The size of the gold particles obtained differs from one support to the other, for instance the diameter of the gold size particles was around 2.3 nm on alumina [74], on the other hand, gold crystal sizes ranging between 2 and 15 nm were obtained on titania [75].
2.6.9 Electrochemical Deposition of Gold Nanoparticles

Electrochemical metal deposition provides a means to prepare metallic nanoclusters on different shapes and areas of conductive substrates. Pulsing techniques have been employed to synthesize small metallic nanoparticles on semiconductors. The main disadvantage of this method is that the particle size dispersion can be large. Ueda et al. [76] have shown that for a double pulsing technique, the crystal nucleation has to occur spontaneously at high current density and the crystal growth has to be conducted at a much slower rate. The time duration of each pulse plays an important role as well. A balance between the pulsing intensity and the duration of the pulse needs to be established in order to obtain highly dispersed, small nanoparticles with little standard deviation of the particles’ diameter. For instance, an increase in the intensity of the first plus or nucleation pulse on the expense of the time duration leads to a decrease in polydispersity of the particles. On the other hand, an increase in the time of the nucleation pulse leads to an increase in the particle density and or the cluster size. The duration of the second pulse of the growth pulse leads to an increase in the particle size. Figure 5 represents a schematic of the potentiostatic double pulse technique [76].
Liu and Juang [77] have prepared gold-coated TiO\textsubscript{2} nanoparticles by electrochemically depositing gold onto titania. Their electrochemical setup consisted of a three-compartment cell, a sheet of gold foil was the working electrode, a KCl-saturated silver-silver chloride (Ag/AgCl) was used as a reference electrode and a platinum foil was used as the counter electrode. They employed a cathod overpotential of 0.82 V versus Ag/AgCl, under sonication and stirring for 1 hour in order to electrochemically synthesize reduced gold nanoparticles on TiO\textsubscript{2}. In order to vary the gold loading, an oxidation-reduction cycles (ORC) was performed, where the working electrode was cycled in a 0.1 N HCl aqueous solution containing 1 mM titania particles, the voltage was varied between -0.28 to +1.22 V versus Ag/AgCl at a rate of 500 mV/s for 10-50 scans. As a result, by increasing the number of scans, the Au coverage on titania reached 95%.

Pérez et al. [78] deposited gold from a N\textsubscript{2} saturated HAuCl\textsubscript{4} aqueous solution with a concentration of 5x10^{-4} M and a pH of three. Similarly, a three-electrode electrochemical
cell was employed. The working electrode consisted of the mesoporous titania film with an exposed area of 0.38 cm$^2$, the counter electrode was a platinum foil, and the reference electrode was a saturated calomel electrode. Prior to gold deposition the working electrode was soaked in the HAuCl$_4$ solution in order for the gold ions to diffuse through the pores of titania. The starting potential was +0.80 V and was stepwised decreased to +0.65 V. The gold electrodeposition was carried out for 2 hours. The average diameter of the gold nanoparticles was around 5.5 ± 0.5 nm, located within the titania pores.
3.0 EXPERIMENTAL

3.1 Substrate and Electrolytes

Indium tin oxide (ITO) glass substrates were supplied by Sigma-Aldrich (8-12 Ω/sq surface resistivity) for the electrosynthesis of TiO$_2$ as well as the gold electrodeposition. These glass substrates were rinsed with acetone as well as deionized water prior to deposition. A copper foil was wrapped around the bottom of the nonconductive side and the edges of the conductive side in order to maintain electrical contact with the electrode. Table 3 contains a list of the chemicals used in the aqueous solution (Deionized water, Fisher Scientific) for the electrosynthesis of TiO$_2$ films [18]. A volume of 500 mL was chosen for the electrosynthesis.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Composition (mol/L)</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanium (IV) Oxysulfate Hydrate (TiOSO$_4$·xH$_2$O)</td>
<td>0.02</td>
<td>Riedel-de Haën</td>
</tr>
<tr>
<td>Hydrogen Peroxide (H$_2$O$_2$)</td>
<td>0.03</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>30 wt% in H$_2$O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitric Acid (HNO$_3$) 70%</td>
<td>0.05</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Potassium Nitrate (KNO$_3$) 99%</td>
<td>0.1</td>
<td>Sigma-Aldrich</td>
</tr>
</tbody>
</table>

Table 3: Electrolyte composition used for the electrosynthesis of TiO$_2$ films

The pH of the solution was maintained at 1.4 and the electrosynthesis was carried out at room temperature. For the gold nanoparticle electrodeposition, a commercially prepared gold solution (TG-25E RTU, ~0.04 M) was supplied by Technic Inc.
A 0.05 M sodium hydroxide (NaOH) aqueous solution was used during the photoelectrochemical testing.

3.2 Electrode Design and Setup

The ITO electrode was submerged in an electrolyte of choice in a 1 L beaker during electrosynthesis of TiO<sub>2</sub> films as well as the electrodeposition of Au nanoparticles. Figure 6 represents a sketch of the electrode holder used. The bottom and the sides of the ITO substrates were wrapped with a copper foil and placed on top of the copper plate in the bottom disc, insulating electrical tapped was placed on the sides of the copper/ITO in order to pin the substrate down to the plate. The top disc has a circular opening and an area of roughly 2.7 cm<sup>2</sup>. The electrode is 1cm deep which helps in establishing a uniform current distribution to the bare surface of the substrate in order to obtain a homogeneous film thickness. O-rings prevent the electrolyte from leaking onto the contact surface and forbid any side reaction from occurring with the copper wrap and plate. The cathode is then seated on top of the copper plate and the top disc is screwed into the bottom. An insulated copper wire is soldered to the base of the bottom disk to supply an electrical connection to the galvanostat or potentiostat. An overall cell schematic is show in Figure 7. A platinum (Pt) wired mesh was used as the anode, placed a few centimeters parallel to the cathode. For the electrosynthesis of titanium dioxide films, a Saturated Calomel Electrode (SCE) was employed as a reference electrode.
Figure 6: Top view (left) and bottom view (right) of the working electrode holder

Figure 7: Schematic of the electrochemical setup
3.3 **Equipments Used for Electrosynthesis/Electrodeposition**

Solartron (SI 1287, Electrochemical Interface) and IM6ex (Zahner Electrik) were used as potentiostats for the electrosynthesis of TiO$_2$ films. A Pine instrument bipotentiostat/galvanostat connected to an AMEL Programmable Function Generator were used for the electrodeposition of Au nanoparticles. A Barnstead Thermolyne 47900 furnace was used to heat treat the titania films. The deposited titania films were weighed with an Analytical Plus (Ohaus) scale.

3.4 **Electrosynthesis of TiO$_2$ Films and Au Nanoparticles**

Cathodic potentiostatic electrosynthesis of titanium dioxide films was performed at room temperature in a three-electrode cell for three consecutive layers. ITO was used as a working electrode (cathode), a Pt mesh was used as a counter electrode (anode) and a SCE was used as a reference electrode. Guided by the work of Georgieva *et al.* [18], the indirect deposition of a hydrous titanium oxo-hydride gel was performed at different applied constant potentials (-1.1 V and – 1.56 V vs. SCE) for one hour followed by a heat treatment at 400ºC/1h. The TiO$_2$ films synthesized at -1.56 V versus SCE was visibly thinner than the one prepared at -1.1 V versus SCE. Furthermore a continuous 3 hour electrosynthesis of titania film at -1.1 V vs. SCE was made followed by a 1 hour heat treatment at 400ºC, resulting in a thin deposit due to the increase in surface resistivity of the gel. The optimum deposition conditions are summarized in Table 4.
Pulsed galvanostatic electrodeposition of gold nanoparticles was performed. A two-electrode cell was employed; the ITO/TiO₂ as a working electrode (cathode) and a Pt mesh as a counter electrode (anode). Most of the pulsed waveforms included a cathodic nucleation pulse followed by a cathodic growth pulse and finally an anodic dissolution pulse. Manipulation of the different pulses resulted in a diversity in the size and density of the gold nanoparticles.

### 3.3 Deposit Characterization

#### 3.3.1 XRD

X-Ray Diffraction (XRD) at the Center for Advanced Microgravity Materials Processing (CAMMP) at Northeastern University was used to characterize the crystallographic structure of the titanium dioxide films. The data was collected using a Cu Kα filtered radiation (40 kV, 30 mA) and a Braker D5005 0:20 Bragg-Brentano diffractometer equipped with a curved graphite crystal diffracted beam monochromator and a NaI scintillation detector. Scanning of the samples was performed between 20 2θ and 60 2θ degrees with a step size of 0.02 degree and 2 seconds/step for a duration of roughly 1 hour.

---

<table>
<thead>
<tr>
<th>Layer</th>
<th>Applied Potential (V) vs. SCE</th>
<th>Duration (h)</th>
<th>Heat Treatment (°C) / Duration (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layer 1</td>
<td>-1.1</td>
<td>1</td>
<td>150 / 1</td>
</tr>
<tr>
<td>Layer 2</td>
<td>-1.1</td>
<td>1</td>
<td>150 / 1</td>
</tr>
<tr>
<td>Layer 3</td>
<td>-1.1</td>
<td>1</td>
<td>400 / 1</td>
</tr>
</tbody>
</table>

**Table 4: Working conditions for the electrosynthesis of TiO₂ films**
3.3.2 SEM and EDAX

Field Emission Scanning Electron Microscopy (S4700 FE-SEM, Hitachi) at the CAMMP was used in order to determine the shape and dimensions of the deposits. Energy Dispersive X-Ray Spectroscopy (EDX) utilizing a phoenix EDAX X-ray analyzer equipped with a sapphire super ultra thin window detector attached to the FE-SEM was used to analyze the elements and their composition. The accelerating voltage of the electron gun was set to 20 kV, the beam current was at 10 µA and the counting time was for 100 seconds.

3.4 Photoelectrochemical Testing

Constant potential, impedance and cyclic voltammetric testings on ITO/TiO$_2$/Au photoanodes were carried out in the dark and under illumination with the CIMPS (Controlled Intensity Modulated Photo Spectroscopy, Zahner Elektrik), IM6ex and PP210 (Zahner Elektrik) in a three-electrode cell equipped with a flat 2 cm diameter quartz window opposite the photoanode (working electrode). The photoanodes were painted with a conductive colloidal silver liquid (Ted Pella Inc.) in order to establish electrical contact with the aluminum binding post. The cell was also equipped with a platinum ring counter electrode and a Ag/AgCl reference electrode. A 1.5 cm diameter O-ring and a plastic plate with a 1.5 cm diameter opening were placed between the O-ring of the cell and the aluminum binding post in order to prevent solution leakage. The distance between the light source and the quartz window is equal to 10 cm. A Polytec/International Light detector is placed 1.7 cm opposite to the photoelectrochemical cell. Figure 8 [79] represents a schematic of the
photoelectrochemical cell and an image of the Zahner CIMPS optical bench. Table 5 [79] includes the type of light sources used as well as their wavelength and maximum available intensity.

Figure 8: Photoelectrochemical cell backside schematic and Zahner optical bench [79]
<table>
<thead>
<tr>
<th>Light Source</th>
<th>Label</th>
<th>Wavelength (nm)</th>
<th>Maximum Intensity (W/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultra Violet</td>
<td>UVZ01</td>
<td>365</td>
<td>37</td>
</tr>
<tr>
<td>Royal Blue</td>
<td>KBL01</td>
<td>455</td>
<td>159.25</td>
</tr>
<tr>
<td>Blue</td>
<td>BLL01</td>
<td>470</td>
<td>234.15</td>
</tr>
<tr>
<td>Cyan</td>
<td>CYL01</td>
<td>505</td>
<td>99.5</td>
</tr>
<tr>
<td>Green</td>
<td>GRL01</td>
<td>530</td>
<td>102.9</td>
</tr>
<tr>
<td>White</td>
<td>WLL01</td>
<td>545</td>
<td>159.25</td>
</tr>
</tbody>
</table>

Table 5: Maximum intensity and wavelength of the employed light sources
4.0 RESULTS AND DISCUSSION

4.1 TiO\textsubscript{2} Electrosynthesis and Characterization

Current density transient curves, Figure 9, were obtained after deposition of each layer. The potential was maintained at -1.1 V versus SCE. The applied potential E is equivalent to the potential difference between the half-cell thermodynamic equilibrium potential, \(E_{\text{rev}}\), and the overpotential, \(\eta\) and includes ohmic losses between the reference and working electrodes,

\[
E - E_{\text{ref}} = E_{\text{rev}} - \eta + IR_{\text{e}} \tag{14}
\]

At steady state the equilibrium potential and the overpotential is not expected to change with time, thus the change of the current density response with time may be due to changes in the ohmic resistance. For a SCE reference, \(E_{\text{ref}} = +0.2412\) V versus NHE (Normal Hydrogen Electrode) [80]. Hence a decrease in the current is observed between each layer which may be due to a subsequent increase in the resistance of the coatings. In all cases the applied potential was equal to -1.1 V versus SCE and the open circuit potential was initially 0.2 V ± 0.1 V versus SCE. The local increase in the solution’s pH at the surface of the electrode led to the indirect deposition of a hydrous titanium oxo-hydrides gel (\(\text{TiO(OH)}_{2}\cdot x\text{H}_{2}\text{O}\)). The oxidation state of Ti did not change throughout the deposition process and remained at +4, hence the electrochemical synthesis induced the deposition of titania through the generation of \(\text{OH}^-\) by the reduction of titanium peroxo-sulfate (\(\text{TiOSO}_4\)).
Figure 9: Current density transient curves generated for three successive layers of TiO$_2$ electrosynthesis with thermal treatment in between each layer.

Figure 10 presents a SEM image revealing a rough and cracked morphology of three layers of TiO$_2$ films with a thin layer of TiO$_2$ visible in between the cracks. The film is made up of patches because of the possible variation of the local pH during the synthesis process, leading to a non-uniform thickness and volume changes of the deposit during the thermal cycles. The drying steps in between each layer result in film shrinkage and cracking. Using an average density for anatase TiO$_2$ equal to 3.894 g/cm$^3$ [81], a planar area of 2.7 cm$^2$, and weighing the mass of the film after deposition of 3 cycles and final drying resulted in a thickness range between 2-3 μm.
Figure 10: SEM micrograph of anatase titania electrosynthesized films (3 layers) revealing a cracked, patch like morphology

Figure 11 shows the XRD patterns of the titania deposits on ITO in Figure 10, as well as bare ITO. The peaks correspond to the anatase crystallographic properties observed in Figure 10 above. The dashed lines are characteristic values for ITO 2θ reflections and the solid lines are the ones corresponding to anatase [82].
Performing electrosynthesis of titania films under ultrasound sonication conditions did not improve the coverage of the sample. Figure 12 reveals a similar morphology to that of Figure 10.

![SEM micrograph of three deposited layers of TiO2 with sonication revealing a cracked morphology and similar thickness to that of Figure 10](image)

**Figure 12**: SEM micrograph of three deposited layers of TiO2 with sonication revealing a cracked morphology and similar thickness to that of Figure 10

4.2 Gold Pulsed Electrodeposition

Deposition of Au nanoparticles on the electrosynthesized TiO2 electrode was obtained using a square-wave, pulsed galvanostatic electrodeposition. Variation of the pulsing parameters affects the size, monodispersity and density of the deposited gold particles.

4.2.1 Constant Charge Pulsing

The mass of the deposits is proportional to the charge passed, once the double layer at the electrode/electrolyte interface is charge. Thus, during each pulse a small fraction of the current is lost to charging the double layer.
Faraday’s law predicts the relationship between the mass deposited and the charge $Q = It$ passed according to
\[ m = \left( \frac{It}{F} \right) \left( \frac{sM}{n} \right) \]  
(15)

where

$m =$ mass of the deposit (g)

$I =$ current (A)

$t =$ time (s)

$F =$ Faraday’s constant 96485 (C/equivalent)

$s =$ stoichiometric coefficient

$M =$ molecular weight (g/mol)

$n =$ number of electrons (equivalent/mole)

Figure 13 represents a schematic of a steady state polarization curve relating the current density ($i$) to the potential at steady state. At low current densities, kinetic control is observed, on the other hand at high current densities, mass transport control takes over and a concentration gradient between the surface of the electrode and the bulk electrolyte exists.
Figure 13: Polarization curve schematic relating current density to potential with mass transport and kinetic control limitations at steady state

Figure A shows that the electrodeposition process reaches a limiting current density right at the mass transport control limit. This maximum current density dictates that the reaction has reached its maximum rate and that any higher applied current may result in side reactions. Overbeek [83] developed a strategy to prepare narrowly dispersed colloid particles as follows: a separation of the nucleation particles from their growth is necessary and achieved with time, and the growth of these particles should be in diffusion control limitation. Two kinds of nucleation could occur, one is called “instantaneous” nucleation and the other “progressive”. Instantaneous nucleation occurs for a short time interval relative to the growth duration and a narrower dispersion in the size of the particles is obtained. Progressive nucleation involves nucleation in the growth period, and a broad size distribution in the size of the generated nanoparticles is likely to occur. Under kinetic control, the particles ideally grow uniform in size thus eliminating “interparticle diffusion coupling” where the depletion layers surrounding neighboring particles overlap. Under diffusion control, interparticle diffusion coupling is most
pronounced since metal ions keep getting depleted at the surface of the electrode and near the surface of the already nucleated particles. Deposition under diffusion control results in a dispersion in the size of the particles since the size of the depletion layer that surrounds them differs from one site to another [84]. Figure 14 [84] represents a schematic about the effect of the deposition of particles under diffusion and kinetic control.

![Figure 14: Effect of the deposition under kinetic and mass transport control on the size dispersion of metal nanoparticles as a function of time [84]](image)

Starting off with the pulsing scheme shown in Figure 15, the constant charge supplied was $3.3 \pm 0.25$ mC/cycle. The total number of cycles was equal to 4. The area of the electrode was $2.71 \text{ cm}^2 \pm 0.05$. 

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Figure 15: Pulsing schematic for Au electrodeposition applying the same charge for 4 cycles

The high current used in the first pulse forces the reduction reaction of metal ion to occur under diffusion control, on the other hand lower currents are indicative of the kinetic control regime. The first pulse is the nucleation pulse, typically the most cathodic one, the next pulse is another cathodic pulse, with amplitude lower than the nucleation pulse and the final pulse is an anodic pulse that causes dissolution of a portion of the deposited gold. The dissolution pulse results in the etching of the formed nanoparticles, rendering them smaller. The resulting Au nanoparticles deposited on TiO₂ films are shown in the SEM micrographs in Figure 16.

Figure 16: SEM micrographs corresponding to the pulsing schemes in Figure 15, left: a), middle: b) and right: c)
By applying a constant charge for electrodepositing gold nanoparticles, one would expect to obtain the same amount of particles deposited. Yet, the SEM micrographs in Figure 16 reveal otherwise. At high applied current nucleation ($I_{nuc}$), and for long time nucleation ($t_{nuc}$), clusters form with an increase in particle homogeneity, Figure 16 (a), where the particle diameter ranged between 20 and 40 nm with approximately 16 particles/µm². A decrease in $t_{nuc}$, Figure 16 (b), and with an additional growth step to maintain constant charge, leads to a slight increase in the particle size (~80 nm diameter), with a decrease in particle aggregation. The particle density was around 13 particles/µm². On the other hand, a larger increasing $I_{nuc}$ and decreasing $t_{nuc}$, leads to discrete small particle (~20 nm diameter) formation with very low density (4 particles/µm²), which correlates well with the results provided by Ueda et al. [76] who found that an increase in the nucleation potential leads to a slight decrease in particle size. They also postulated that the particle density is highly dependent on the parameters of the first pulse or nucleation pulse and that $I_{nuc}$ and $t_{nuc}$ must achieve a certain maximum to achieve nucleation. On the other hand, to suppress particle growth, these parameters should not exceed a certain maximum.

4.2.2 Variation in the Number of Cycles

Another parameter that has been investigated was the number of cycles performed. Figure 17 represents a pulsing schematic performed for 1 cycle and 4 cycles.
Figure 17: Pulse schematic for Au electrodeposition performed for 1 cycle and 4 cycles

Figure 18 includes SEM images taken for 1 pulsing cycle and 4 pulsing cycles for the same nucleation, growth and dissolution pulses. For a single cycle, particles with diameter ranging between 50 and 150 nm and 5 particles/µm² were observed. Repeating the cycle four times resulted in clusters with ~80 nm diameter with more distance between each cluster. Clusters form even in the first cycle and particle size dispersion is not well controlled since small particles as well as larger ones are formed. This effect could be due to the fact that the nucleation pulse is in the kinetic control region where distribution narrowing does not occur. Instead, growth at diffusion or mass transport control as a function of time encourages smaller size distribution as smaller particles grow and catch up to larger ones [86]. Nanoparticles with 100 nm diameter and clusters with 120 to 200 nm diameter were observed in Figure 18 c) with a density of 2 particles/µm². Moreover, Figure 18 c) shows that clusters form even during the first pulse (-33 mA, 25 ms). The growth step in the cycle is thus not responsible for the clustering, it is the nucleation step that is key.
Figure 18: a), b): effect of the number of cycles on particle size and cluster formation. c): Cluster grow in size without dissolution pulse. d): clusters form right after the first pulse

The effect of the number of cycles was also investigated with respect to a higher nucleation pulse. Figure 19 represents a schematic of the pulsing conditions and Figure 20 corresponds to SEM micrographs taken of the prepared samples with different deposition cycles.
In Figure 20, the particles grew in size with increasing the number of cycles, yet the particle density was not much affected. In Figure 20 (a) the particle diameter size was 20 nm, in Figure 20 (b) the particles had a diameter range between 30 and 50nm and a density of 2 particles/µm², and for the largest number of cycles (Figure 20 (c)), the particle diameter was between 50 and 100 nm with 1 particle/ µm². This could be possibly due to the fact that instantaneous nucleation takes place at high pulsing and in order to increase the particle density, longer nucleation time should be employed.
4.2.3 Variation in Nucleation Time

Figure 21 illustrates a schematic of three different pulsing schemes performed for 4 cycles each, where the nucleation time has been varied while keeping the applied currents constant for the nucleation, growth and dissolution pulses. The growth time and the dissolution time were also kept constant for all three pulsing schemes. Figure 22 provides SEM micrographs for the three different pulsing techniques. In scheme c) of Figure 21, the current was set to zero for 0.05 ms between every high pulse. This rest time should theoretically result in the disappearance of any formed small particles with a radius smaller than the critical radius of a gold nanoparticle, thereby resulting in a narrower size distribution [76].

![Schematic of pulsed schemes](image)

**Figure 21:** Effect of nucleation time on particle size and density. Each deposition was performed for 4 cycles.

![SEM micrographs](image)

**Figure 22:** SEM micrographs corresponding to the pulsing schemes apparent in Figure 21, left: a), middle: b) and right: c)
Figure 22 (a) is the same micrograph shown in Figure 20 (a) and compared to other different schemes. In Figure 22 (b), the size of the particle diameter around 75 nm, with agglomerates and smaller particles around 30 nm diameter and 5 particles/µm². Increasing the nucleation time resulted in an increase in the size of the particles and the formation of clusters. In Figure 22 (b) and (c), the density of Au nanoparticles increased (7 particles/µm²) and smaller ones emerged (20 nm). This is characteristic of a progressive nucleation.

A final variation in the nucleation time as shown in Figure 23, also resulted in an increase in the particle density (38 particles/µm²) and dispersion in size (20-40 nm diameter). Particles between 20 – 40 nm diameter were visible and large particle agglomerates evolved.

![Pulsing scheme and SEM micrograph for a nucleation time of 36 ms, the deposition was performed for 4 cycles](image)

**Figure 23:** Pulsing scheme and SEM micrograph for a nucleation time of 36 ms, the deposition was performed for 4 cycles
4.2.4 Effect of the Growth Pulse on Particle Density and Size

Another parameter that was investigated with respect to the electrodeposition of Au on TiO₂ was the growth pulse. In Figure 24, the growth pulse was omitted resulting in the formation of larger particles with less size dispersion. Figure 24 also provides an SEM micrograph where the formation of large clusters is observed with wider interparticle distance. The range of the particle diameters was between 20 and 40 nm with formation of large clusters around 120 nm diameter and a particle density of 13 particles/μm².

![Figure 24: Pulsing scheme and SEM micrograph with omission of growth pulse performed for 4 cycles](image)

This again shows that the first pulse plays a detrimental role in determining the particle size and density. A comparison between Figure 23 and Figure 24 reveals that the growth pulse mainly influences the number of isolated particles where an increase in the growth time leads to a decrease in the number of solitary particles. Liu and Penner [86], suggested that for particles to grow independently from one another, the nucleation time must be less than the coalescence time of the depletion layer when under transport.
control. In other words, the depletion layers for neighboring particles should not fuse together. The concentration of a spherical metal particle as a function of the radial distance can be written as [86,87]

\[
C(r) = C^* - \frac{(C^* - C_0)r}{r}
\]  

(16)

where \(C^*\) is the concentration of the metal ion in the bulk, \(C_0\) is the concentration at \(r_0\), the surface of the cathode and \(C_0\) ranges between 0 and \(C^*\). In the limit of kinetic control, when the concentration at the surface of the electrode or when \(C_0\) is equal to \(C^*\), no depletion layer exists and the particles grow independently of one another [86]. This technique can be implemented by reducing the overpotential of the growth of metal particles, hence reducing the growth rate. This can be done experimentally by applying a short duration but high potential or current nucleation pulse followed by a growth pulse with a value much less than that of the nucleation potential and a duration greater than that of the nucleation time [84]. In most of the cases presented above, the growth pulse was low enough but not long enough, resulting in cluster formation. Furthermore, the pulsing was repeated for 4 cycles. This could be a reason why the results generated deviated from what Penner [84] had suggested.

EDAX spectra were obtained for several samples and mostly showed similar intense Ti peaks and broad Au peaks due to the relatively small size of the gold nanoparticles. Figure 25 provides an EDAX spectrum of Au nanoparticles placed on a TiO\(_2\) film. The small peak around 200 KeV is representative for the detection of gold and elemental sulfur. The electrolyte used for the electrodeposition of Au includes sulfides. The presence of sulfur on the titania films is not surprising since the electrolyte
contains sulfites. Moreover an increase in the photoelectrochemical behavior of TiO₂
doped sulfur has been reported [57,61] and is expected to have a beneficial effect.

![Figure 25: EDAX spectra of TiO₂/Au sample, Au was electrodeposited at
-66.7 mA for 36 ms followed by a dissolution pulse of
0.05 mA for 20 s, performed for 4 cycles, with peaks of
Ti, Au and S](image)

4.2.5 Au Electrodeposition Through Membrane

Using a membrane to deposit Au nanotube arrays has been investigated. One
sample has been prepared to create a regular, uniform distribution of gold nanoparticles
on the surface of the titania films. The pulsed galvanostatic deposition was as follows
and for 1 cycle:

-3.44 mA, 25 ms

-0.95 mA, 350 ms

This resulted in the formation of gold nanoparticles, spherical in shape with a narrow size
distribution of particle diameter due to the fixed diameter of the pore (50 nm) and a particle density of 2 particles/µm². Figure 26, represents SEM micrographs of the deposits.

![SEM micrographs of Au nanoparticles prepared by pulsed electrodeposition through a membrane](image)

**Figure 26:** SEM micrographs of Au nanoparticles prepared by pulsed electrodeposition through a membrane

### 4.3 Buried Au Nanoparticles in a TiO₂ Matrix

Burying Au nanoparticles within nanometers of the titania surface may introduce local defects within the titania matrix. These defects should play an important role with respect to enhancing the absorption range of TiO₂, hence causing a red-shift. Furthermore, these defects play a crucial role in enhancing the injection and separation of the photogenerated electron/hole pairs. Moreover, by placing the Au nanoclusters between the two layers of titania should protect the metallic clusters from oxidation or corrosion. After preparing 3 layers of TiO₂ and laying Au nanoparticles on top of them, a top layer was electrosynthesized. The deposition potential was equal to -1.1 V versus SCE and the time duration lasted for 7, 10 and 30 min for different samples.

The absorption coefficient of titania is equal to 4 x 10⁴ cm⁻¹ at 380 nm wavelength
and $10^5$ cm$^{-1}$ at 348 nm \cite{81}. Based on these properties, the absorption length of TiO$_2$ subjected to UV light was calculated to in the $1/(1 \times 10^5)$ to $1/(4 \times 10^4) = 0.25$ to $0.1$ μm range. A thickness of 113 ± 0.5 nm was obtained for the electrosynthesis of titania top layer for a duration of 10 min followed by a heat treatment at 400°C. The deposit thickness in all cases is greater than the absorption length of titania, which implies that most of the incident UV light is absorbed by the as prepared photoanodes.

Another variation of these generated TiO$_2$/Au sandwiched samples included the placing of Au nanoparticles on top of the top layer of titania. Figure 27 represents an illustration of buried Au nanoparticles within the titania matrix and on top of it.

Figure 27: Schematic illustrating buried metallic Au clusters within TiO$_2$ matrix resulting in a disruption of the matrix and additional Au particles placed on top.

Figure 28 includes a SEM micrograph illustrating the representative of the schematic in Figure 27. The top layer was electrosynthesized at -1.1 V for 10 min and heat treatment at 400°C for 1 h was then performed. The gold nanoparticles in between the layers and
on top were deposited at -33.4 mA for 25 ms and -10 mA for 350 ms for 1 cycle each. The gold electrodeposition resulted in particles with ~40 nm diameter.

![SEM micrograph of Au nanoparticles deposited on top of 3 bottom layers and 1 top layer of titania with Au nanoparticles in between](image)

**Figure 28:** SEM micrograph of Au nanoparticles deposited on top of 3 bottom layers and 1 top layer of titania with Au nanoparticles in between

Photoelectrochemical characterization of these samples was performed. Different light sources corresponding to different wavelengths were employed to test the photoresponse of the prepared samples. In addition, dynamic transfer function tests with light modulation as well as impedance spectra were obtained.

### 4.4 Photoelectrochemical Characterization

#### 4.4.1 Photocurrent Response

The photocurrent generated with a semiconductor is indicative of the dynamics of the photogenerated electrons and hole, and of the kinetics associated with the semiconductor/electrolyte reactions. Figure 29 illustrates a schematic of a band diagram of an n-type semiconductor [88]. Upon illumination of a photoanode, a photocurrent is generated as a result of electron/hole pairs created and separated within the depletion layer of width \( W \) [88]. The depletion layer of the space charge layer is defined as the
layer in which the majority charge carriers, the electrons in an n-type semiconductor, are being removed. Whereas, the minority charge carriers or holes, migrate to the surface of the electrode participating in the redox reactions [89]. The penetration depth of the light $L(\lambda)$ is defined as the reciprocal of the absorption coefficient $\alpha$. Due to the effective charge separation within the space charge region, the concentration of holes at the bulk edge is relatively low. $L_p$ is the distance over which, the minority carriers can diffuse through in order to reach the depletion layer edge and eventually the semiconductor/electrolyte interface [88].

![Band diagram](image)

**Figure 29**: Band diagram where a depletion layer is shown at the n-type semiconductor/electrolyte interface

The presence of grain boundaries, electrical interactions between the photoexcited electrons and dipole molecules in the electrolyte and trapping of electrons in the band
gap, increases the photocurrent generation [88]. Surface recombination of holes and electrons can be described as follows [90]

\[ R^* + h^+(VB) \rightarrow R^+ \]  \hspace{1cm} (17)

\[ R^+ + e^-(CB) \rightarrow R^* \]  \hspace{1cm} (18)

Where \( R^* \) is a recombination center in the bandgap that can trap a hole from the valence band (VB) and generate \( R^+ \). \( R^+ \) can then capture an electron from the conduction band (CB) and restore \( R^* \).

Upon irradiation of the photoanode, an increasing negative shift in the open circuit potential (OCP) is observed reflecting an increase in the steady-state concentration of electrons in the titania conduction band [4]. Figure 30 provides a graph indicative of the evolution of the open circuit potential upon illumination of a gold modified photoanode Figure 18 (c). In the dark the OCP is around -0.21 V vs. Ag/AgCl. Upon illumination of a UV light source at a constant intensity of 30 W/m² the OCP decreases to a range between -0.325 and -0.391 V vs. Ag/AgCl. When the light is turned off, it takes the OCP ~400 s to stabilize and get back to its original value.
Figure 30: Modification of the OCP upon irradiation of the photoanode in 0.05 M NaOH with UVZ01 (365 nm wavelength) at 30W/m²

Photoexcitation of the electrodes leads to a photocurrent generation. Electrons and holes contribute to the photocurrent evolution. The transfer of both electrons and holes to the back contact is conceivable. If the electrons are the main carriers injected into the back contact, then an anodic photocurrent is observed. On the other hand, a cathodic photocurrent is detectable if holes are mainly injected [4].

4.4.1.1 ITO and ITO/Au

Photoelectrochemical tests on bare ITO and ITO/Au were performed. Figure 31 represents the response of the electrodes due to UV irradiation. The Au nanoparticles were deposited at -33 mA for 25 ms and the second pulse was at -10 mA for 350 ms for 1 cycle on ITO.
As indicated, for the ITO/Au sample the light was switched on and off for several intervals. A small anodic photocurrent was observed, probably due to the fact that ITO is an oxide itself and that Au placed on top could possibly increase its response. On the other hand, bare ITO electrodes show no response to UV irradiation.

4.4.1.2 Pristine TiO₂

Photocurrent measurements were performed on bare TiO₂ electrodes. The electrolyte in use was 0.05 M NaOH. Na⁺ ions are suspected to likely help in shielding the electrons stored in Au particles. This shielding helps in preventing electron/hole recombination in nanostructured semiconductor TiO₂ cells [91]. Most of the measurements were carried out at OCP where there is no net change in the electrochemical reaction. Upon irradiation of the electrode which is being maintained at OCP the pronounced increased in photocurrent is then only due to the response of the sample to light excitations. Furthermore, at OCP or the zero current potential, there is a minimal driving force for the collection of photogenerated electrons at the electrode [11]. Figure 32 represents a photocurrent response to several light source excitations. The potential was maintained at OCP and all the tests were performed on the same day.
As expected, pristine titania is only responsive to UV irradiation or shorter wavelength than ~365 nm. The maximum photocurrent generated is ~2.5 µA. Upon turning the light on, a sharp increase in the photocurrent was observed (~100 s), followed by a decay after the light was turned off (~300 s).

Figure 33 corresponds to a photocurrent response when the ITO/TiO₂ electrode was subjected to different applied potentials. At higher positive bias, an increase in the photocurrent is observed because of an enhancement in the charge separation. This effect is due to the fact that the kinetic factors that influence the hole transfer at the
semiconductor/electrolyte solution are what dictate the electron accumulation within the semiconductor film [16].

**Figure 33:** Photocurrent response of ITO/TiO₂ electrodes maintained at different potentials, (1) dark OCP (-0.33 V) and (2) +0.1 V vs. Ag/AgCl

More than a 10 time increase in photocurrent was observed with an increase of applied potential from OCP to +0.1 V versus Ag/AgCl.

**4.4.1.2 TiO₂/Au**

Figure 34 shows the photocurrent response of the sample from Figure 16 a). The potential was maintained at dark OCP in a 0.05 M NaOH solution.
Figure 34: Photocurrent response of ITO/TiO$_2$/Au electrode in 0.05 M NaOH solution with potential maintained at dark OCP = -0.38 V vs. Ag/AgCl

A very low photocurrent increase was detected upon illumination of the electrode and this could be mainly due to the large Au nanoparticles on top of titania, resulting in blocking the active site of the catalyst. No anodic photocurrent response was detected with royal blue and green light sources.

Figure 35 represents the photocurrent response of the prepared sample shown in Figure 18 c), with Au nanoparticles (~100 nm diameter) electrodeposited with a pulse at -33 mA for 350 ms and a growth pulse at -10 mA for 350 ms for 1 cycle, under UV excitation maintained at dark OCP.
Figure 35: Photocurrent response to UV irradiation of ITO/TiO$_2$/Au electrode in 0.05 M NaOH maintained at dark OCP: (1) -0.257 V, (2) -0.266 V and (3) -0.206 V vs. Ag/AgCl

In this case, each test was at the OCP conditions and the more repetitive the test the more there was a decrease in the observed photocurrent. Figure 36 represents the photocurrent response of the electrode upon light irradiation with different wavelengths of the same sample Figure 18 c). The electrode was maintained at dark OCP in a 0.05 M NaOH solution. The blue light sources KBL01 was used at two different intensities, 30 W/m$^2$ and 200 W/m$^2$. The green light source GRL01 was used at 30 W/m$^2$. 
A response to longer wavelengths than 365 nm was observed with ITO/TiO$_2$/Au electrodes. This represents a shift in the photoelectrochemical response to the visible region. Furthermore, an increase in the intensity of the light source led to an increase in the photocurrent and this is due to the optical nonlinearity of gold nanoparticles on titania [56]. Figure 37 corresponds to the photocurrent response of the sample shown in Figure 18 c) under UV irradiation at different applied potentials: dark OCP, +0.1 and +0.3 V versus Ag/AgCl.
Figure 37: Photocurrent response to UV irradiation in 0.05 M NaOH maintained at different potentials: (1) dark OCP = -0.266 V, (2) $E = +0.1$ V and (3) $E = +0.3$ V vs. Ag/AgCl.

Similar to ITO/TiO$_2$ electrodes, the photocurrent increased with increasing applied potentials. Figure 38 includes photocurrent versus time curves performed on the same sample (Figure 18 c)) a couple of months later.
A noticeable decrease of the photocurrent response was observed after retesting the sample. Initially, the photocurrent was higher (25 µA, 14 µA/cm²) (Figure T), dropping to 1 µA, 0.46 µA/cm². The curves in Figure 38 labeled (2) and (3) correspond to tests performed consecutively on the same day, curve (1) corresponds to a test ran a couple of days later than (2) and (3). This decrease in the photocurrent could be possible due to the oxidation of Au nanoparticles that have a large surface/volume ratio. These nanoparticles can therefore be affected by the UV light or undergo corrosion at the semiconductor interface by holes or OH⁻ [56].
the same conditions as the sample shown in Figure 18 c); gold electrodeposition: -33.4 mA for 25ms and -10 mA for 350 ms for 1 cycle. The particles diameter ranged between 100 – 150 nm.

The tests (1) and (2) were performed on the same day. A large decay was observed for test (1). On the other hand, test (2) was more stable with a maximum photocurrent ~6 µA, 3 µA/cm². In both cases the photocurrent response was much less than the one shown in Figure 35. This decrease may be due to the fact that the original sample represented in Figure 18 c) was prepared seven months before the light testing was performed.

Figure 39: Photocurrent response to UV irradiation at 30 W/m² of a duplicate of sample show in Figure 18 c) in 0.05 M NaOH at dark OCP: (1) +0.039 V and (2) -0.087 V vs. Ag/AgCl
Figure 40 represents photocurrent tests of the sample shown in Figure 20 a) with UV irradiation. The Au nanoparticles (~20 nm diameter) were electrodeposited with a pulse at -66 mA for 12 ms, followed by growth pulse at -10 mA for 350 ms and a dissolution pulse at +0.05 mA for 20 s for 4 cycles. The sample showed no response to royal blue and green light irradiation (not included in graph).

Curve (2) corresponds to the second test performed and shows a better response than curve (1). Both tests were performed on the same day. Figure 41 includes photocurrent response curves to UV irradiation of the same sample tested above (Figure 20 a)). These tests were performed four days after the initial ones apparent in Figure 40.
A small decrease in the photocurrent response was detected after the initial tests shown in Figure 40.

Figure 42 includes photocurrent response of the sample shown in Figure 20 b) under UV irradiation. The Au nanoparticles (~50 nm diameter) were electrodeposited with a pulse at -66 mA for 12 ms, followed by growth pulse at -10 mA for 350 ms and a dissolution pulse at +0.05 mA for 20 s for 60 cycles. Only one UV test was performed and the sample was not responsive to royal blue or green light irradiation.
Figure 42: Photocurrent response to UV irradiation of sample shown in Figure 20 b) in 0.05 M NaOH at dark OCP: +0.047 V vs. Ag/AgCl

Figure 43 corresponds to photocurrent response of sample shown in Figure 20 c) under UV irradiation. The Au nanoparticles (~80 nm diameter) were electrodeposited with a pulse at -66 mA for 12 ms, followed by growth pulse at -10 mA for 350 ms and a dissolution pulse at +0.05 mA for 20 s for 120 cycles.
Figure 43: Photocurrent response to UV irradiation of sample shown in Figure 20 c) in 0.05 M NaOH at (1) dark OCP: +0.007 V, (2) -0.002 V and (3) -0.008 V vs. Ag/AgCl (3).

A small decrease is also observed with increasing the number of tests performed. No response to royal blue or green light irradiation was obtained.

Figure 44 represents the photocurrent response of Figure 20 a), b) and c) under UV irradiation. The Au nanoparticles were deposited at -66 mA for 12 ms followed by a growth pulse at -10 mA for 350 ms and a dissolution pulse at +0.05 mA for 20 s for 4, 60 and 120 cycles respectively. The increase in the number of cycles led to an increase in the particle diameter size and not in the particle density.
The photoresponse was not affected by the number of cycles that increased the Au nanoparticle size. All three sample show similar behavior with a photocurrent response of 6.5 µA, 3.6 µA/cm².

Figure 45 represents the photocurrent response of the sample shown in Figure 24 under UV irradiation. The Au nanoparticles (~20 - 40 nm diameter) were electrodeposited with a pulse at -66 mA for 36 ms, followed a dissolution pulse at +0.05 mA for 20 s for 4 cycles.
A small photocurrent response in the nanometer range was detected. The sample showed a lower photocurrent value less than that of bare TiO$_2$.

Figure 46 represents the photocurrent response of the sample shown in Figure 26 under UV irradiation. The Au nanoparticles (~50 nm diameter) were electrodeposited with a pulse at -3.44 mA for 25 ms, followed by growth pulse at -0.95 mA for 350 ms for 1 cycle.
Figure 46: Photocurrent response to UV irradiation of sample shown in Figure 26 in 0.05 M NaOH at dark OCP: (1) -0.083 V and (2) +0.052 V vs. Ag/AgCl

The photocurrent reached a maximum then decayed in both cases. This again proves that having particles with narrow size distribution does not necessarily enhance the photocatalytic activity of TiO$_2$/Au composites.

4.4.1.3 ITO/TiO$_2$/Au/TiO$_2$

Sandwiched Au nanoparticles in between the titania layers samples were subjected to photoelectrochemical tests. The samples were prepared as follows and in the same order as shown below

a) TiO$_2$ electrosynthesis:

layer 1: -1.1 V versus SCE for 1h, followed by drying at 150°C for 1h
layer 2: -1.1 V versus SCE for 1h, followed by drying at 150°C for 1h
layer 3: -1.1 V versus SCE for 1h, followed by heat treatment at 400°C for 1h

b) Au electrodeposition for 1 cycle:
   -33 mA for 25 ms
   -10 mA for 350 ms

c) TiO₂ top layer electrosynthesis:
   -1.1 V versus SCE for either 10 (sample a) or 30 min (sample b), followed by
   heat treatment at 400°C for 1h.

Figure 47 corresponds to the photoresponse of the sandwiched sample under UV
irradiation in 0.05 M NaOH. The top layer was electrosynthesized for 30 min at -1.1 V
versus SCE (sample b). The sample showed no response to royal blue and green light
excitation. Curves (1), (2) and (3) were tests maintained at OCP under UV illumination,
performed in the same labeling order.
Figure 47: Photocurrent response of TiO$_2$/Au/TiO$_2$ to UV irradiation in 0.05M NaOH maintained at different potentials, sample (b): (1) dark OCP = +0.176 V, (2) +0.148 V and (3) -0.147 V vs. Ag/AgCl, (4) E = +0.3 V vs. Ag/AgCl

All four tests were performed on the same day. A 2 µA, 1 µA/cm$^2$ response was observed for tests conducted under dark OCP. By applying an external potential of +0.3 V versus Ag/AgCl a higher step photocurrent response was detected, ~4 µA.

A second sample was tested were the top layer was electrosynthesized for a shorter time of 10 min at -1.1 V versus SCE (sample a). Figure 48 corresponds to the photocurrent response of the sample under UV irradiation in 0.05 M NaOH at dark OCP.
Unlike the sample with a top layer electrosynthesized for 30 min (Figure 47), this one exhibited a small photoresponse under royal blue irradiation with a maximum around 460 nA, 260 nA/cm$^2$. The sample underwent further tests four days after the initial ones shown in Figure 48. Figure 49 includes these restest, where the electrode was submerged in 0.05 M NaOH and irradiated with different light sources: UV and royal blue.

**Figure 48:** Photocurrent response to different light sources in 0.05 M NaOH, sample (a): UVZ01 30 W/m$^2$: dark OCP = (1) +0.173 V and (2) +0.101 V vs. Ag/AgCl, KBL01 200W/m$^2$: (3) dark OCP = +0.058 V vs. Ag/AgCl (3)
The later tests presented in Figure 49, showed similar response to UV irradiation, with a stable photocurrent around 10 µA, 5.6 µA/cm² (curve 2). A repeat of the royal blue test resulted in a decrease of the previously recorded photocurrent (~460 nA, Figure 48), attaining a maximum of 300 nA, 170 nA/cm². No photoresponse was obtained with green light irradiation. A top layer electrosynthesized for 10 min instead of 30 min showed a significant photocurrent increase under UV irradiation and a response under royal blue illumination. This effect could be mainly due to the fact that the 10 min electrosynthesized top layer is thinner than the 10 min one, where the electrons would travel a shorter distance to reach the Au nanoparticles and then make their way to the back contact.
4.4.1.4 ITO/TiO$_2$/Au/TiO$_2$/Au

Following the same setup as in section 4.4.1.3 for the electrosynthesis of Au nanoparticles within titania layers, additional gold nanoparticles were then electrodeposited on top of the top layer. The gold electrodeposition consisted of the following galvanostatic pulses for 1 cycle:

-33 mA for 25 ms
-10 mA for 350 ms

Figure 50 includes photocurrent responses of sample (b), section 4.4.1.3 (30 min top layer at -1.1 V versus SCE) in addition to gold on top under UV irradiation in 0.05 M NaOH.

![Figure 50: Photocurrent response of sample (b) with Au on top under UV irradiation in 0.05 M NaOH at dark OCP = (1) -0.024 V and (2) -0.026 V vs. Ag/AgCl](image_url)
A photocurrent increase was observed compared to Figure 47, but it was followed by a decay.

Figure 51 includes photocurrent response of sample (a) section 4.4.1.3 (10 min top layer at -1.1 V versus SCE) with gold nanoparticles on top (~100 nm diameter) electrodeposited with a pulse at -33 mA for 350 ms and a growth pulse at -10 mA for 350 ms for 1 cycle, under UV irradiation in 0.05 M NaOH.

![Figure 51: Photocurrent response of sample (a) with Au on top under UV irradiation in 0.05 M NaOH at dark OCP = (1) -0.055 V, (2) -0.056 V and (3) -0.034 V vs. Ag/AgCl](image)

A sharp increase in the photocurrent response reaching a value of ~50 µA, 28 µA/cm² (curve (1)) was observed followed by a decrease. Curves 2 and 3 show a more stable photocurrent response at lower values, 16 µA, 9 µA/cm² (2) and 13 µA, 7 µA/cm³ (3). Retests of the sample shown in Figure 51, are presented in Figure 52. The tests were
performed under UV irradiation in a 0.05 M NaOH and 1 M NaOH after 3 days of the initial tests shown in Figure 51.

The photocurrent response was stable (12 µA, 6.7 µA/cm²) (curve (2)) in 0.05 M NaOH. This value is within close proximity to the one obtained in Figure 51. On the other hand, with increasing the molarity of the NaOH solution to 1, a higher stable response was observed (21 µA, 11.8 µA/cm²) (curve (3)). The reason could be related to the increase in the OH⁻ ions that capture the holes generated on the semiconductor/electrolyte interface, hence decreasing the recombination rate.

A thinner top layer corresponding to a deposition time of 7 min was tested. Au nanoparticles were electrodeposited on the top layer with pulsing for 1 cycle at

Figure 52: Retesting the photocurrent response of sample (a) with Au on top under UV irradiation at dark OCP = (1) -0.026 V, (2) -0.012 V vs. Ag/AgCl in 0.05 M NaOH and (3) -0.015 V vs. Ag/AgCl in 1 M NaOH
-33 mA for 25 ms
-10 mA for 350 ms

Figure 53 includes the photocurrent response of the sample under UV irradiation in 0.05 M NaOH. The sample was not tested under royal blue or green light excitation.

Figure 53: Photocurrent response with UV irradiation in 0.05 M NaOH at dark OCP = (1) -0.180 V and (2) -0.190 V vs. Ag/AgCl

In Figure 53, a decrease in the photoresponse compared to samples (a) (10 min top layer at -1.1 V versus SCE) and (b) (30 min top layer at -1.1 V versus SCE) was detected.

Figure 54 includes photocurrent response plots of (1) bare TiO₂, (2) TiO₂/Au (Figure E c)), Au nanoparticles (~100 nm diameter) electrodeposited with a pulse at -33 mA for 350 ms and a growth pulse at -10 mA for 350 ms for 1 cycle, (3) TiO₂/Au/TiO₂ with a top layer electrosynthesized for 10 min at -1.1 V versus SCE and TiO₂/Au/TiO₂/Au also with a top layer electrosynthesized for 10 min at -1.1 V versus
SCE and Au nanoparticles (~100 nm diameter) electrodeposited with a pulse at -33 mA for 350 ms and a growth pulse at -10 mA for 350 ms for 1 cycle. The electrodes were submerged in 0.05 M NaOH and irradiated with UV light at 30 W/m².

![Figure 54: Photocurrent response with under UV irradiation in 0.05 M NaOH of different samples at dark OCP = (1) -0.33 V, (2) -0.226 V, (3) +0.173 V and (4) -0.516 V vs. Ag/AgCl](image)

The sample with Au nanoparticles on top deposited at -33 mA for 25 ms and -10 mA for 350 ms for 1 cycle (curve 2), showed the highest photocurrent response (20 μA, 11 μA/cm²) to UV irradiation with an intensity of 30 W/m². The next best photoresponse was observed for the sandwiched Au nanoparticles in between titania layers with Au nanoparticles on top, where the top titania layer was deposited at -1.1 V versus SCE for 10 min (curve 4, 17 μA, 9.6 μA/cm²). Shielding the Au nanoparticles with a top layer of
titania resulted in a lower response (curve 3, 11 µA, 6 µA/cm²). All three samples showed a higher photocurrent step response under UV irradiation than bare TiO₂ (curve 1).

4.5 **Impedance Analysis**

Electrochemical Impedance Spectroscopy (EIS) involves a sinusoidal alternation of the applied potential, at low amplitudes, where the system will be linear with respect to current and potential. Measurements were conducted with an ac component $\Delta E_\omega$ passed through the working electrode:

$$\Delta E_\omega = \Delta E_m \sin \omega t$$  \hspace{1cm} (19)

$$\omega = 2\pi f$$  \hspace{1cm} (20)

where

- $E_m$ = amplitude of the applied potential
- $\omega = \text{angular frequency} = 2\pi f$; $f$ is the ac frequency

In an electrochemical impedance experiment the frequency is varied in order to probe different processes that have different time constants. Figure 55 [80] represents a schematic of a simplified equivalent circuit for a metal used to interpret impedance measurements of a metal.
If an electrode were to behave as a pure ohmic resistance, the relation between the change in potential and the instantaneous value of intensity will be

\[
\frac{\Delta E}{\Delta I} = \frac{E_m}{I_m} = R_\Omega \tag{21}
\]

This ideal situation does not exist in real electrodes, on the other hand, a phase shift (\(\alpha\)) appears between alternating current and alternating potential. In electrochemical systems, the current changes can lag, lead or be in phase with the potential changes

\[
\Delta E = \Delta E_m \sin(\omega t - \theta) \tag{22}
\]

which can be represented by different simple electric circuit elements. The impedance is characterized by the modulus

\[
|Z| = \frac{\Delta E_m}{\Delta I_m} \tag{23}
\]

and the phase shift \(\theta\) [80].

There are two ways to represent the data. One method is called the Nyquist plot. It is a diagram where the imaginary part of Z is plotted versus the real part of Z. Another
representation is called the Bode plot, which is a composite of two figures, one log $|Z|$ is plotted versus log $\omega$ and the other is $\theta$ versus log $\omega$, where [22]:

$$\left[ Z \mp \text{Re}(Z)^2 + \text{Im}(Z)^2 \right]^{1/2} \quad (24)$$

$$\theta = \tan^{-1}\left( \frac{\text{Im}(Z)}{\text{Re}(Z)} \right) \quad (25)$$

Figure 56 represents a schematic of a Nyquist plot illustrating the different resistances presented in Figure 55, often used to depict the processes occurring at one electrode verses a reference.

![Nyquist plot](image)

**Figure 56**: Typical shape of a Nyquist plot with: a) charge transfer and double layer limitations at the high frequency range, and b) mass transport limitation at the low frequency range. The intercept with Re(Z) is $R_\Omega$

The different impedances present in Figure 55 can be equated as follows

$$Z = Z_\Omega + \left[ \frac{1}{Z_{d.l.}} + \frac{1}{Z_{c.t.} + Z_{m.t.}} \right] \quad (26)$$
At high frequency the capacitive effect behaves as a closed circuit and the response is that of only an ohmic resistance, having no imaginary component. At the other extreme, at low frequency the capacitive component acts like an open circuit and the impedance response is reflected of all the resistances in series: ohmic, charge transfer and diffusion. Diffusion is a slower process than charge transfer and so manifests itself at the lowest frequency. If the diffusion layer is not fixed, but changes with time, then the response is a straight line on the Nyquist plot at 45° angle. If the capacitive effect dominates this is a vertical line on the Nyquist plot, in the imaginary plane. Typically charge transfer and capacitive effects occur at similar frequencies and this combination creates a semi-circular response [22].

The following impedance plots were generated by modulating the applied potential in a sinusoidal manner. The electrode was submerged in a 0.05 M NaOH solution with UVZ01 light source irradiating it.

Figure 57 represents a Nyquist plot of bare TiO₂ in dark and under UV irradiation in 0.05 M NaOH. The impedance is highest at the low frequency end and decreases approaching a real impedance value at high frequency.
Figure 57: Impedance measurements in dark and in light of bare TiO$_2$ in 0.05 M NaOH at dark OCP = +0.035 V vs. Ag/AgCl ± 20 mV with 500 mHz < f < 3 MHz

Both measurements, in the dark and in the light, resulted in identical plots, where a capacitive effect was observed at low frequencies and ohmic resistance is found at high frequency since the imaginary component goes to zero.

Figures 58, 59, 60 and 61 illustrate Nyquist plots of the sample shown in Figure 18 c), with Au nanoparticles (~100 nm diameter) at different applied steady-state potentials in the NaOH electrolyte. The Au was electrodeposited on the ITO with a pulse at -33 mA for 350 ms and a growth pulse at -10 mA for 350 ms for 1 cycle. The tests were performed in dark and under UV irradiation. The potentials varied from the value at
dark OCP: -0.081 (Figure F4) to biased potentials in the anodic direction of, +0.1 V (Figure 59) and +0.3 V (Figure F6) versus Ag/AgCl. All of them are compared in Figure 61.

![Graph showing impedance measurements in dark and light of Au/TiO₂ in 0.05 M NaOH at OCP = -0.081 V vs. Ag/AgCl ± 10 mV with 100 mHz < f < 3 MHz]

At low frequencies, a vertical line was observed indicative of capacitive effects. In that particular region, the interface behaves as a pure capacitor. At higher frequencies, the plot starts taking the shape of a semicircle which is characteristic of the kinetic control region.
Figure 59 represents a Nyquist plot of the same sample at +0.1 V versus Ag/AgCl in dark and under UV irradiation in 0.05 M NaOH. A similar shaped was observed to that of Figure 58. Kinetic control effects as well as capacitive effects dominate the process under study in dark and under irradiation.

Figure 59: Impedance measurements in dark and in light of Au/TiO₂ in 0.05 M NaOH at E = +0.1 V vs. Ag/AgCl ± 10 mV with 100 mHz < f < 3 MHz

Figure 60 represents a Nyquist plot of the same sample at an even larger positive potential of +0.3 V versus Ag/AgCl in dark and under UV irradiation in 0.05 M NaOH.
Similar observations to that made to Figures 58 and 59 were obtained, where capacitive and kinetic control effects take place.

Figure 60: Impedance measurements in dark and in light of Au/TiO$_2$ in 0.05 M NaOH at $E = +0.3$ V vs. Ag/AgCl ± 10 mV with 100 mHz < $f$ < 3 MHz

Figure 61 represents a comparison between different impedance measurements performed under different applied potentials in dark and under UV irradiation in 0.05 M NaOH on the sample shown in Figure 18 c). The plot shows that they all superimpose with a similar capacitive feature. Thus, the enhancement in the reaction with UV light is not due to the capacitive affect between the interfacial solid and solution phase, and that the differences in the reaction must be due to the solid phase.
The plots of Figure 61 superimposed, showing no difference in the impedance spectra generated under irradiation and in the dark, at OCP or with applied external bias. At low frequencies, the system acted as a pure capacitor, and at high frequencies, charge transfer and ohmic resistances were dominant.

Figures 62, 63, 64 and 65 represents Nyquist plots of a sandwich deposit of TiO$_2$/Au/TiO$_2$ film (sample a), section 4.4.1.3) (10 min top layer at -1.1 V versus SCE), with Au nanoparticles (~100 nm diameter) electrodeposited with a pulse at -33 mA for 350 ms and a growth pulse at -10 mA for 350 ms for 1 cycle in 0.05 M NaOH in dark and
under UV irradiation. These plots differ in the same manner as in the previous impedance plots, the applied steady-state potential is varied.

Figure 62 shows the result when the steady-state applied potential is +0.028 V vs. Ag/AgCl which corresponds to the OCP in the dark. Curve (1) is the response in the dark and curve (2) is the response when the electrode is irradiated. Unlike the previous case, when gold sits on the surface of TiO$_2$, there is a difference in the response with and without UV irradiation. Thus, there is a shift in the governing process of the electrochemical anodic reaction in the NaOH. The impedance curves in light and in dark show similar shapes, the shapes are characteristic of a kinetic-capacitive effect. There is also a decrease in the impedance values due to illumination, which suggests a faster charger transfer, or in other words a lower $R_{ct}$ at the electrode-solution interface.
Figure 62: Impedance measurements in (1) dark and in (2) in light of TiO$_2$/Au/TiO$_2$ in 0.05 M NaOH at dark OCP = +0.028 V vs. Ag/AgCl ± 10 mV with 100 mHz < f < 3 MHz

Figure 63 represents the Nyquist plot of the sandwich at a higher applied steady-state potential of +0.1 V versus Ag/AgCl in dark and under UV irradiation in 0.05 M NaOH. Curve (1) is the response in the dark and curve (2) represents the response under UV irradiation. Similar shaped curves to those in Figure 62 were obtained, indicating the presence of kinetic-capacitive effects. Similarly, a decrease in the impedance under irradiation, suggestive of a faster charge transfer process was also observed.
Figure 63: Impedance measurements in (1) dark and (2) in light of TiO$_2$/Au/TiO$_2$ in 0.05 M NaOH at $E = +0.1$ V vs. Ag/AgCl ± 10 mV with 100 mHz $< f < 3$ MHz

Figure 64 represents a Nyquist plot of the sandwich at +0.3 V versus Ag/AgCl in dark and under UV irradiation in 0.05 M NaOH. Similar shaped curves to those obtained in Figure 62 and Figure 63 are shown here. These curves represent kinetic-capacitive effects taking place in dark and upon illumination. Furthermore, the impedance response under illumination decreased more than at dark OCP and +0.1 V vs. Ag/AgCl, indicative of an even faster charge transfer process.
Figure 64: Impedance measurements in (1) dark and (2) in light of TiO$_2$/Au/TiO$_2$ in 0.05 M NaOH at $E = +0.3$ V vs. Ag/AgCl ± 10 mV with 100 mHz $< f < 3$ MHz.

Figure 65 represents a comparison between different impedance measurements performed under different applied potentials in dark and under UV irradiation in 0.05 M NaOH. In general, there is a decrease in the charge transfer resistance when the light is applied since the impedance value is smaller than that in dark conditions. This decrease in the charge transfer resistance is proportional to an increase in the reaction rate the photocurrent response. In dark, an increase in the applied steady-state potential leads to a decrease in the impedance values. This latter effect is observed when a certain electrochemical reaction is purely driven by an increase in the applied potential. In other words, a higher applied potential results in more rapid reactions. On the other hand,
under illumination, no shift was visible when the potential changes from dark OCP (+0.028 V) and +0.1 V versus Ag/AgCl. A more pronounced decrease in the impedance at +0.3 V versus Ag/AgCl was obtained.

Figure 65: Impedance measurements in Figures: 62, 63 and 64 dotted lines represent the dark electrode and the solid lines are the irradiated cases. (1) dark OCP = +0.028, (2) E = +0.1 V, (3) E = +0.3 V, (4,5) dark OCP = +0.028 V and E = +0.1 V, and (6) E = +0.3 V vs. Ag/AgCl

Since the shape of the Nyquist plots have changed between having the gold on TiO₂ and the sandwiched gold between the TiO₂, the limiting factor controlling the reaction has changed. There is a shift from a capacitive feature to one where both kinetics and capacitance play a role. Furthermore, the impedance under UV illumination has a
smaller affect than that in the dark, for the downward shift observed in dark at different applied potentials is bigger than that in light.

4.6 IMPS Characterization

Intensity modulated photocurrent spectroscopy (IMPS) gives insight into understanding the kinetics and mechanisms participating in the photoelectrochemical reactions occurring at the semiconductor/electrolyte interface [92]. Modulating the light intensity in an n-type semiconductor, results in the modulation of the density of holes in the valence band [90]. Similar to EIS, the sinusoidal modulation of light is small so that the response in current is sinusoidal, in other words the system is linear. Experimental results presented in this section are all linear. Some high frequencies examined did result in a noisy response and a loss of linearity. All noisy data were omitted.

Figure 66 [92] represents a schematic of a simplified equivalent circuit for a semiconductor used to interpret intensity modulated photocurrent spectroscopy measurements. The equivalent circuit that was previously presented, Figure 55, did not reflect light sensitive processes within the semiconductor. When the light is modulated, not just always on or off, the impedance can detect changes in these light sensitive processes. The surface state capacitance (C_{ss}) and the surface state resistance (R_{ss}) represent the region at the boundary of the solid at the edge of the depletion layer. The Helmholtz capacitance, C_{H}, describes the double layer region that develops in the solution, existing at the semiconductor/electrolyte interface. The space charge region capacitance, C_{SC} is highly influenced by illumination of the electrode. It is typically smaller or comparable than the Helmholtz capacitance [92,93].
Figure 66: Equivalent circuit representation employed for IMPS analysis

Figure 67 represents a schematic of an IMPS plot [94], where charge transfer and surface recombination data can be obtained from the first quadrant, for the special case when the electrochemical reaction resistance is very high compared to the resistance at the semiconductor surface. The low-frequency limit of the differential steady-state photocurrent increase, indicted as $I_1$, is due to a differential increase in the light intensity [94]. The other intercept, $I_2$, represents the amplitude of the Gärtner flux $g$, indicative of the flux of minority carriers to the electrode surface [95]. The amplitude ($A$) and the phase shift ($\phi$) for different modulating frequencies of the light source ($\omega$), are also included on the plot [94]. Moreover, the frequency at the apex of the semicircle ($f_{\text{max}}$), is equivalent to $\tau^{-1}$, where $\tau$ is the surface-recombination time constant [90].
Figure 67: Typical shape of an IMPS plot in the complex plane, $f_{\text{max}}$ corresponds to the highest frequency modulation, located at the top of the semicircle [94]

Figure 68, represents a complex IMPS plot of bare TiO$_2$ in 0.05 M NaOH at different applied potentials, under UV irradiation with modulation of the light source. The generated data points located in the fourth quadrant implies that the resistance, R, at the semiconductor/solution interface [92] is small, thus charge transfer is fast. There is a negative imaginary impedance component so the response is also a result of the space charge and Helmholtz capacitors in parallel with the charge transfer resistance.
Figure 68: IMPS response of bare TiO$_2$ in 0.05 M NaOH at different potentials: dark OCP = +0.035 V, +0.1 V and +0.3 V vs. Ag/AgCl. Light source: UVZ01 30 W/m$^2$, 100 mHz $< f < 1$ kHz and an amplitude of +0.02 V

Figure 69, represents a complex IMPS plots of TiO$_2$/Au corresponding to Figure 18 c), in 0.05 M NaOH solution at different applied potentials, under UV irradiation with modulation of light intensity. The generated plots were located in the first quadrant of the complex IMPS plot, which indicates that the charge transfer and the electron/hole recombination was the limiting process [92]. At dark OCP and at +0.3 V under UV irradiation, $\omega_{\text{max}}$ is equal to 126 Hz, resulting in a $\tau$ constant equal to 0.00126 s. At +0.3 V, $\tau$ is equal to 0.001 s.
Figure 69: IMPS response of Au/TiO$_2$ in 0.05 M NaOH at different potentials: (1) dark OCP = -0.081 V, (2) +0.1 V and (3) +0.3 V vs. Ag/AgCl (3). Light source: UVZ01 30 W/m$^2$, 100 mHz < $f$ < 1 kHz and an amplitude of +0.02 V.

Figure 70 represents a complex IMPS plot of TiO$_2$/Au/TiO$_2$ (sample a), section 4.4.1.3) (top layer electrosynthesized at -1.1 V versus SCE for 10 min). The IMPS response of the sandwich electrode in 0.05 M NaOH at different applied potentials, under UV irradiation with modulation of the light source shows a similar behavior as in bare TiO$_2$, but with larger photocurrent. The generated plots were located in the fourth quadrant of the complex IMPS plot, which indicates that the electrochemical reaction
occurring at the semiconductor/electrolyte interface was the limiting process [92].

Figure 70: IMPS response of TiO$_2$/Au/TiO$_2$ in 0.05 M NaOH at different potentials: dark OCP = +0.028 V, +0.1 V and +0.3 V vs. Ag/AgCl. Light source: UVZ01 30 W/m$^2$, 100 mHz < $f$ < 3 MHz and an amplitude of +0.02 V

Figure 71 represents a complex IMPS plot of TiO$_2$/Au/TiO$_2$/Au (sample a) (top layer electrosynthesized at -1.1 V versus SCE for 10 min), section 4.4.1.3 with Au nanoparticles on top ((~100 nm diameter) electrodeposited with a pulse at -33 mA for 350 ms and a growth pulse at -10 mA for 350 ms for 1 cycle). The IMPS response is
given for different applied potentials, under UV irradiation with modulation of the light source, as in Figures 69 and 70.

The generated plots were located in the first and fourth quadrants of the complex IMPS plot, which indicates that the charge transfer and the kinetics of the electrochemical process are influenced by the applied potentials and the modulation frequency.
reaction were equally controlling [92]. The value of $\omega_{\text{max}}$ is equal to 16000 Hz, resulting in a $\tau$ equal to $9.97 \times 10^{-6}$ s.

A direct comparison between the sample with gold on top (Au/TiO$_2$) of Figure 69 and the sandwich with Au on top (TiO$_2$/Au/TiO$_2$/Au) of Figure 71, shows that the electron life time for the former is longer than that of the later. This result is further solidified by Figure 54, where the photocurrent response of the Au/TiO$_2$ is higher than that of the TiO$_2$/Au/TiO$_2$/Au sample.
5.0 CONCLUSIONS

The purpose of this present work was to electrosynthesize both titania and gold nanoparticles in order to test the composite’s photoelectrochemical activity towards water splitting reactions and subsequent hydrogen evolution. Titania films with an average thickness ranging between 2-3 µm were electrosynthesized via cathodic electrodeposition from a TiOSO₄ and H₂O₂ acidic electrolyte on ITO glass substrates. The process involved the indirect electrodeposition of a hydrous titanium oxo-hydrides gel, morphing into crystalline anatase after heat treatment. The gold nanoparticle electrodeposition was carried out using a commercially prepared solution. Pulsed waveform galvanostatic electrodeposition at different applied currents for different time durations was employed in order to obtain surface bound gold nanoparticles. The size and the particle density varied from one waveform to another. Photoelectrochemical tests confirmed that particle density and dispersion is more important than particle size with respect to increasing the photocurrent response. The concept of buried Au nanoparticles within nanometers of the titania surface was also investigated. Gold nanoparticles sandwiched between titania layers were thought to introduce local defects within the TiO₂ matrix. These defects were believed to play an important role with respect to enhancing the absorption range of titania, hence causing a red-shift in the photoresponse. Another variation of the sandwich samples included the electrodeposition of Au nanoparticles on top of the sandwich. Photoelectrochemical tests, including step photoresponse analysis under different light sources, impedance analysis and intensity photo modulated current spectroscopy techniques were employed to characterize the enhanced photoelectrochemical response of the prepared samples. The samples were submerged in 0.05 M NaOH and the
photoanodes were biased under different applied potentials. Results have shown that electrodepositing gold on titania resulted by the highest photocurrent response and the red-shifting of the photoresponse of the photoexcited composite. The second best photoresponse was obtained with the TiO$_2$/Au/TiO$_2$/Au samples, where the top layer was electrosynthesized at -1.1 V versus SCE for 10 min and the Au nanoparticles were electrodeposited at -33 mA for 25 ms and -10 mA for 350 ms. The third best photoresponse compared to pristine titania was with the sandwiched Au nanoparticles in between 3 bottom layers of TiO$_2$ and 1 top layer (electrodeposited at -1.1 V versus SCE for 10 min). Moreover, aging effects and additional rigorous photoelectrochemical tests resulted in a decrease in the photocurrent response of the tested samples. In most cases, the highest photocurrent response value was observed during the first test. Electrodepositing Au on TiO$_2$ resulted in photocurrent responses under royal blue and green light excitations, indicating a red-shift of the photoresponse. On the other hand, pristine TiO$_2$ was only responsive to UV (λ ~ 365 nm).
6.0 RECOMMENDATIONS

This work is consistent with other literature findings that Au nanoparticles on TiO$_2$ can enhance the reaction rate of the anodic reaction in water splitting; it is the first study where both the TiO$_2$ and Au are both fabricated electrochemically. Further work should be directed towards optimizing the electrodeposition parameters. Different waveform pulse should be investigated consisting of other applied currents and time durations. Electrochemical pulses can be used to alter nucleation and growth mechanisms which dictate the size and shape of the Au nanoparticles and TiO$_2$ film. Another fruitful direction is to control the distribution of Au nanoparticles on TiO$_2$ with the use of nanoporous membranes. A single study was carried out in this direction with promising results. In addition, the use of nanoporous membranes make possible the fabrication of gold nanotube arrays or nanorods and it would be interesting to study their photoelectrochemical response.

Methods resulting in higher surface area titania films need to be studied and implemented. These methods include the electrochemical fabrication of TiO$_2$ nanorods or nanotubes with different lengths and wall thicknesses.

Sandwiched nanoparticles of different noble metals could be a promising technique to further red-shift the photoresponse of the TiO$_2$/metal composite. Placement of metal nanoparticles on top of the sandwich different than the ones within the titania matrix could result in different electronic states localized on the surface of the semiconductor film as well as in the bulk. These changes may further enhance the photoresponse under UV irradiation and potentially other wavelengths.
The incorporation of dyes in the semiconductor has been well studied with improved 
TiO₂ photoelectrochemical properties. Combining the dyes with the composite materials 
could be promising. The dyes would absorb photons from a range of light sources, 
extended into the visible range and eventually injected the excited electrons into the 
semiconductor. The noble metals should facilitate the transport of these newly injected 
electrons to the other electrode and prevent their trapping within the energy states of the 
semiconductor.

Titania has been renowned to be a non-hazardous and cheap material for water 
splitting reactions, on the other hand, it has limited capabilities since it only responds to 
UV irradiation. Other types of semiconductor materials need to be researched and 
investigated in hopes to generate a material with high photoelectrochemical efficiencies.
7.0 REFERENCES


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