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作品編號 100041

參展科別 工程學

作品名稱 Bifunctional Nanostructured TiO₂
photoelectrocatalyst for Improving
Overall Water splitting performance

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Abstract:

Titanium dioxide TiO_2 is a semiconductor, that has great chemical and physical properties, such as remarkable resistance against corrosion, chemical stability, and it's a non-toxic material. Due to these properties, it rises as an excellent candidate for a wide range of different applications, such as being a popular material for solar cells, paints, cosmetics, energy storage devices, and water splitting. For photoelectrochemical water splitting to generate Hydrogen, a large surface area is essential, to be maximized to enhance photocatalytic redox processes and hence improve overall efficiency. Therefore, different methods have been utilized to fabricate TiO_2 nanotubular structure. However, they either encounter a difficult process because of a long synthesis time or the need of expensive precursors. In our work, we demonstrated a study of enhancing 1 D TiO_2 film to perform as a bifunctional catalyst (works as cathode and anode). As it is known that TiO_2 is kinetically hampered as cathode for producing hydrogen from water, this is due to sluggish electron transfer at the interface between TiO_2 and water and the conduction band of the TiO_2 , which is more negative than H^+/H_2 . To tackle this problem, TiO_2 film should be modified. In this work, we modified the TiO_2 as bifunctional by investigating different parameters in detail, like the anodic oxidation solution content, anodic oxidation time, and the role of the polyethylene glycol chain. Electrochemical characterization and SEM, and XPS were utilized to prevent the nanotubes structure and to confirm the chemical bonding as well as investigating the physical properties such as resistance and electron kinetic mobility.

Introduction:

Titanium dioxide TiO_2 is a semiconductor, that has great chemical and physical properties, such as an excellent resistance against corrosion, chemical stability, and non-toxic material. These features make it a wide range candidate for different applications, such as popular material for solar cells, paints, cosmetics, energy storage devices and water splitting. TiO_2 has three form meta-stable phases of rutile ($E_g=3\text{ eV}$), brookite and anatase ($E_g=3.2\text{ eV}$), the anatase is the most popular form that has been used in different applications, due to nanoscale-size crystallite that comes from

the surface energy impact. Whatever, TiO_2 suffers from main types of problems that limits its application in photoelectrochemical water splitting, i) it has a huge band gap and limits its absorption of visible light and can only absorb UV light, ii) fast recombination of photo generated electron-hole pairs, which electron at CB can recombine quickly with holes at VB and lose energy as unproductive heat or photons, iii) quick reversible reaction can occur, thus hydrogen and oxygen recombine again easily. However, an ideal TiO_2 that enhances and promotes water splitting performance should be addressed and considered all above problems either by addition of electron donors, doping, or noble metal loading etc. For photoelectrochemical water splitting a huge surface area is also crucial to be maximized for enhancing the photo catalytic redox reactions and thus enhancing the overall efficiency. Therefore, different methods have been utilized to TiO_2 nanotubular structure, but they either suffer from a long synthesis time or the need of expensive precursors. Thermal methods are widely used to fabricate TiO_2 , spraying, sol,gel, chemical/physical deposition and hydrothermal. By thermal oxidation a thick oxidation layer of TiO_2 has been formed and leading to thick barrier, making an isolated layer between Ti substrate and the oxide layer. This leads to recombination losses, because the barrier can prevent or affect electron transfer to the metal electrode thus the reduction of water become less active. To solve TiO_2 obstacles, anodic oxidation was chosen to oxidize the Ti foil at room temperature, and with controlling all oxidation parameters (working electrode area, oxidation media content, time, potential, ...), a 1D TiO_2 nanostructure (nano tube, nanowires) can be formed. 1D nanotube is one of the perfect structures that form from anodic oxidation with excellent optimization film quality such as high surface area, great catalytic reaction performance and efficiency. Moreover, the charge carrier transportation becomes faster and enhancing the water splitting reaction because of unidirectional electrical channel that might alter the electronic properties owing to quantum size effects' strong contribution of surface reconstruction or surface curvature. In our work we demonstrated a study of enhancing 1 D TiO_2 film to work as bifunctional material (works as cathode and anode). As known that TiO_2 is kinetically hampered as cathode for producing hydrogen from water, this is due to sluggish electron transfer at the interface between TiO_2 and water and the conduction band of the TiO_2 is more negative than H^+/H_2 . To tackle this problem, TiO_2 film should be modified, for example noble metal co-catalysts, specifically Au, Ru and Pt, that can allow a fast extraction of the excited electron from TiO_2 , but these metals are precious. Magnéli modified TiO ($2n-1$) ($n=4-37$), it is chemically inert and has semi-metallic properties

possessing electrical behavior and has good stability for water splitting. In this work we modified the TiO_2 as bifunctional (as cathode and anode) by study in details some parameters (anodic oxidation solution content, anodic oxidation time and the role of the polyethylene glycol chain and the distance between working electrode and counter electrode).

Hypothesis:

TiO_2 has a large energy band gap (3.0 eV) resulting in a very limited portion of solar light (4%–5%) being captured and utilized. As well as a fast recombination rate of photogenerated charges. Furthermore, TiO_2 is known to work well as anode in photoelectrochemical water splitting and it is kinetically hampered as cathode for producing hydrogen from water, this is due to a sluggish electron transfer at the interface between TiO_2 and water and the conduction band of the TiO_2 which is more negative than H^+/H_2 . Here in this work, we are looking to fabricate 1D nanotubes TiO_2 by anodic oxidation and modify its physical and chemical properties to obtain an excellent bifunctional photocatalyst where we also focus on the cathode reduction reaction in PEC water splitting.

Experimental:

Materials

Titanium Ti foil (99.95%, T 0.1mm), Ethylene glycol 99% (EG) EMPLURA, Ammonium fluoride 98% NH_4F Sigma Aldrich, Acetone 99% Honeywell, Ethanol 96% Honeywell, Potassium hydroxide 85% Honeywell, Sulfuric Acid 98% BDH.

Ti Foil anodic oxidation

Anodic oxidation is the electrochemical method for oxidize the Ti foil to TiO_2 and to form and control the oxidation layer thickness on the foil surface. This method has several advantages such creation and controlling the tubular internal and external length, size and shape by controlling anodic oxidation electrical voltage, time, oxidation time, and oxidation bath content and concentration. Before Ti foil oxidation the foils were ultrasonically clean with, acetone, ethanol and DI water for 5 min each and left to dry. The anodic solution contents of (NH_4F (0.14gm, 52

g Ethylene glycol and 3 gm DI water), a platinum mesh electrode was used as counter and cleaned Ti (1cmx2cm) as anode. The voltage was kept a constant at 60V by CPX400S 420W DC Power Supply instrument, distance between working electrode and counter has measured and kept constant for all experiment (3cm) except for optimizing the distance experiment (1-9) cm. (fig 1)

Instrumentations

A Field Emission Scanning Electron Microscope (FESEM; Tescan Lyra-3) was used to study the morphology of the Ti foil treated samples. (X-ray photoelectron spectroscopy Thermos-Scientific) was used to study the chemical composition.

Electrochemical characterization

Electrochemical experiments were performed with an Autolab PGSTAT204 (Metrohm, UK) controlled with Nova software). Water-oxidation, water reduction and overall water splitting of modified Ti/TiO₂ samples were investigated by linear sweep voltammetry (LSV), chronoamperometry and electrochemical impedance spectroscopy (EIS). Electrochemical impedance spectroscopy (EIS) analysis was carried out at different overpotentials in the frequency range of 100 kHz - 50 mHz with a 10 mV ac amplitude. Three electrode configuration cell (a three-electrode system with a Ti/TiO₂ as working electrode, a Standard Pt Counter Electrode, 6.9 mm OD epoxy tube shroud (for water oxidation) Standard Graphite Counter Electrode, 6.4 mm OD, 12 mm OD glass (for water reduction) as counter electrode, and Ag/AgCl as reference electrode in in 1 M KOH (water oxidation) and (1 M H₂SO₄ (water reduction) at scan rate 5 mVs⁻¹, all potentials were referred to reversible hydrogen electrode (RHE) by calibration to (RHE) using the following Equations: $E(\text{RHE}) = E(\text{Ag/AgCl}) + 0.241 + 0.059 \text{ pH}$.

Results and discussions

To understand the formation process of TiO₂ oxide layer growth on Ti foil, several parameters have been investigated and, the surface has been studied thoroughly by SEM and XPS. It is widely known that contents of the electrolyte have a vital impact in synthesizing well-defined nanotubes and fine tuning its properties. The electrolyte has three main contents water, fluorine content

material, and organic material (EG). The electrolyte must contain water molecules, which serves as an essential source of oxygen molecules during the anodization process. Additionally, it plays a significant role in hastening the dissolution of the nanotube layer. The main condition of water in the electrolyte solution is having small water quantities, which hampers the oxygen availability thus reducing overall oxidation growth and chemical dissolution. Another role of the water is to control the tubes splitting as it dissolves the F-containing anodic TiO_2 . The third main containing material in the electrolyte, is the Ethylene glycol as the organic compound that has a significant impact on increasing the efficiency of growth rate, it found that the growth rate increases 750-6000 % higher when organic material has been used, rather than other polar organic or aqueous electrolyte, due to the high viscosity and its contribution for extending the tubes length and controlling the tubes order and smoothing the morphology of the tube wall.

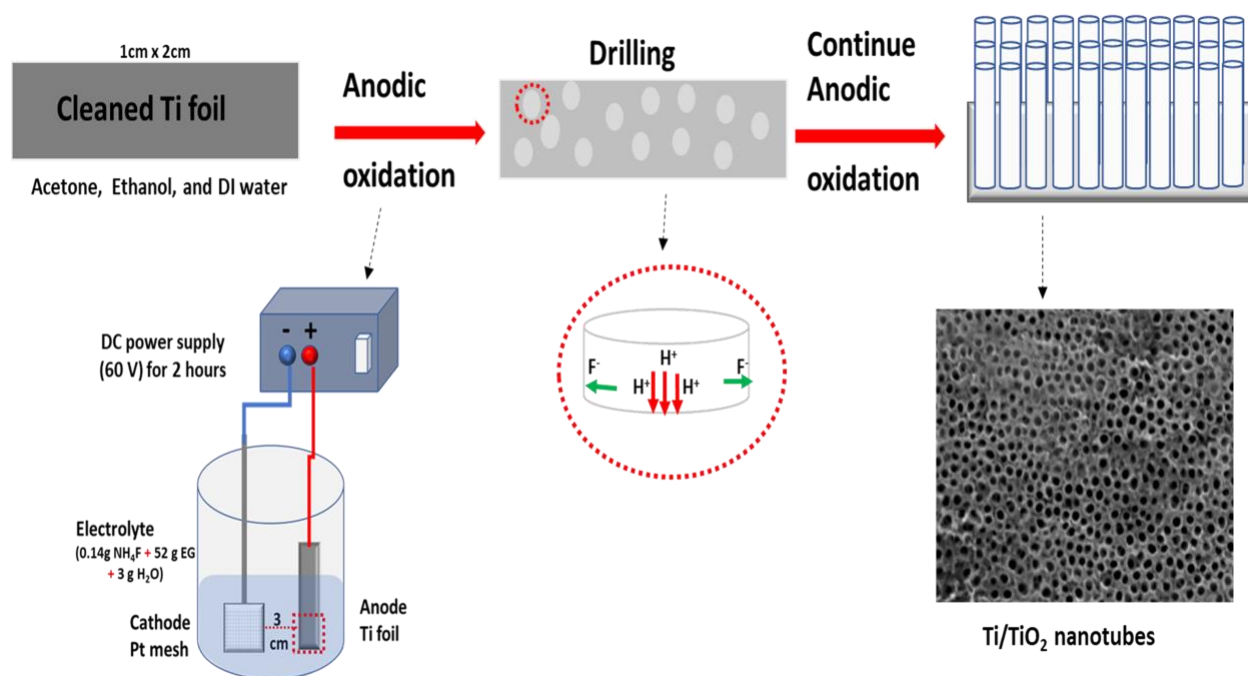


Figure 1, illustration for experimental set up and the role of NH_4F and ethylene glycol.

In the synthesis of the TiO_2 nano tubes, a NH_4F was used for controlling the surface morphology. Ti foil works as anode and Pt mesh as cathode, at Pt an electronation is formed $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$. At anode the Ti dissolves in the parallel with water electrolysis and O_2 is released, and pH is changed

due to electrochemical reaction of anodic oxidation. At this stage, TiO_2 , $\text{Ti}(\text{OH})_4$ are accumulated on the surface. During anodic oxidation F with acidic media can play an important role for Ti surface chemical etching in presence of O_2^- or OH^- species and, electrochemically anions such F^- and cations (protons and titanium cations) diffuse to or from the metal-oxide interface. F can incorporate with TiO_2 and form water soluble $[\text{TiF}_6]^{2-}$ species that activate the pores on Ti surface to control and maintain the bottom growth of the tubes by chemical etching. Moreover, the TiO_2 can undergo chemical dissolution and form Ti^{4+} complexes at the oxide electrolyte interface. The anodic oxidation of titanium foil can be occurred as followed:[8], [9], [10], [11], [12], [13]

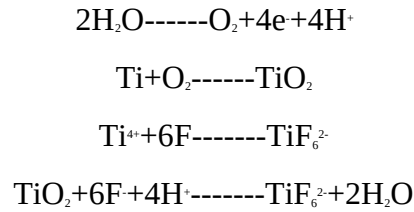


Figure 2 illustrates the role of anodic oxidation time on the morphology of Ti foil using the EG, water and NH_4F for electrolyte content and all parameters were kept constant such as the electrolyte concentration, anodic oxidation voltage and the distance between two electrodes, only the anodic oxidation time was changed in the range of (1-4) hour. The anodic oxidation time is an essential parameter for formation and controlling the nanotubes and also it affects the pores size of the tubes, r formation and controlling the nanotubes and also it affects the pores size of the tubes, from SEM it's clear that less than 2h the nanotubes had formed but not on all the surface, the pore sizes are smaller than higher anodic time, at 2h a perfect structure with uniform dispersion of nanotubes were obvious and no residual impurities were found, when the anodic oxidation time increases to 3h the morphology of the nanotubes destroyed and no pattern was noticed, when the anodic oxidation extended to 4h we can observed some nanotubes with large opened pores.

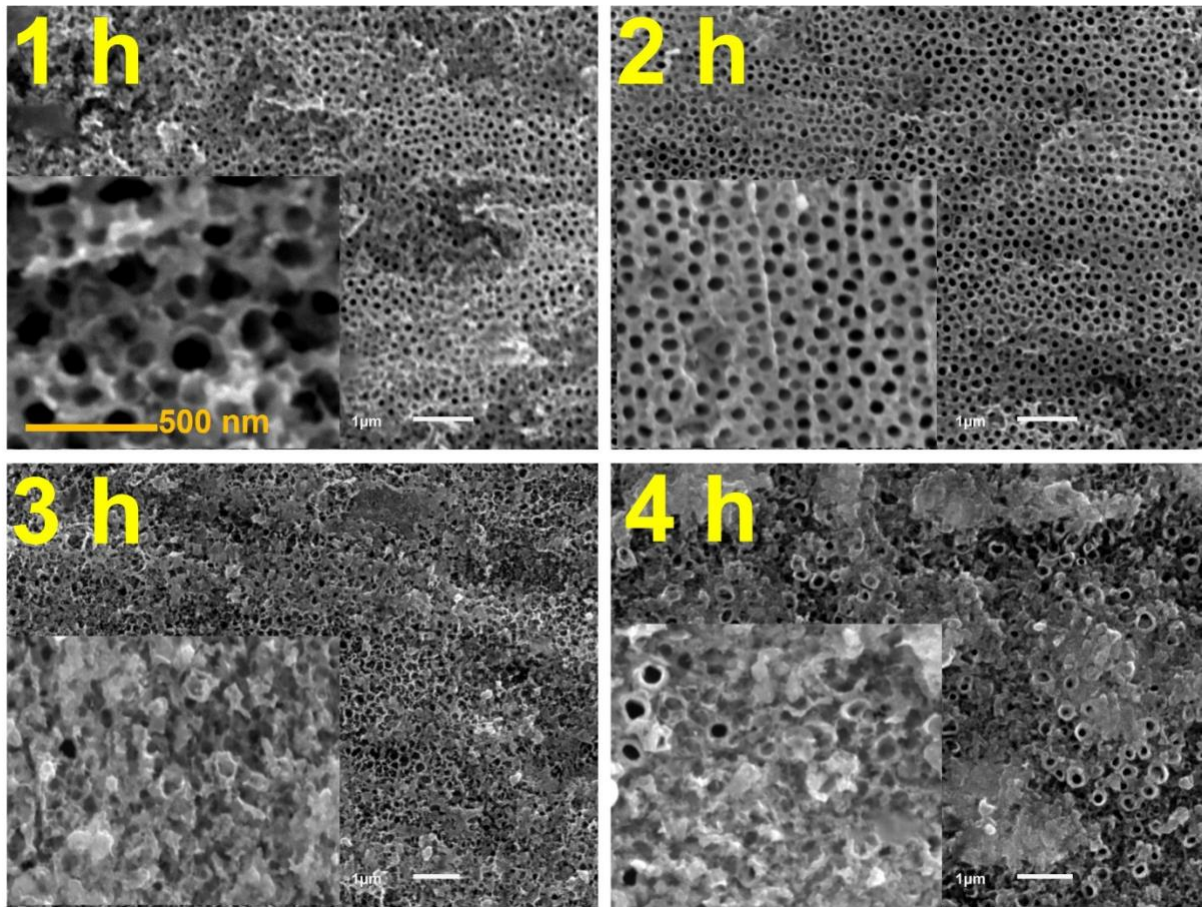


Figure 1, Scan electron microscopy (SEM) for anodic oxidation of the Ti foil at (a) 1h, (b) 2h, (c) 3h, and (d) 4h using electrolyte solution

Flat band potential of all prepared samples at different anodization time were investigated by measuring electrochemical impedance spectroscopy. Figure 4 presents all the Mott Schottky plots for all samples to identify conductivity type of semiconductor; for clean Ti foil a positive slope was obtained demonstrating the n-type electronic nature of the Ti foil sample. All other samples that were anodized at different anodization times show straight lines with both positive and negative slopes suggesting that TiO_2 -t samples have the characteristic features for n-type and p-type. Ti vacancies can introduce a p-type behavior to the TiO_2 samples as well known that since the concentration of metal vacancies is high enough the p-type can be detected. While both oxygen vacancies and metal interstitials are shallow donor that response for n-type conductivity.

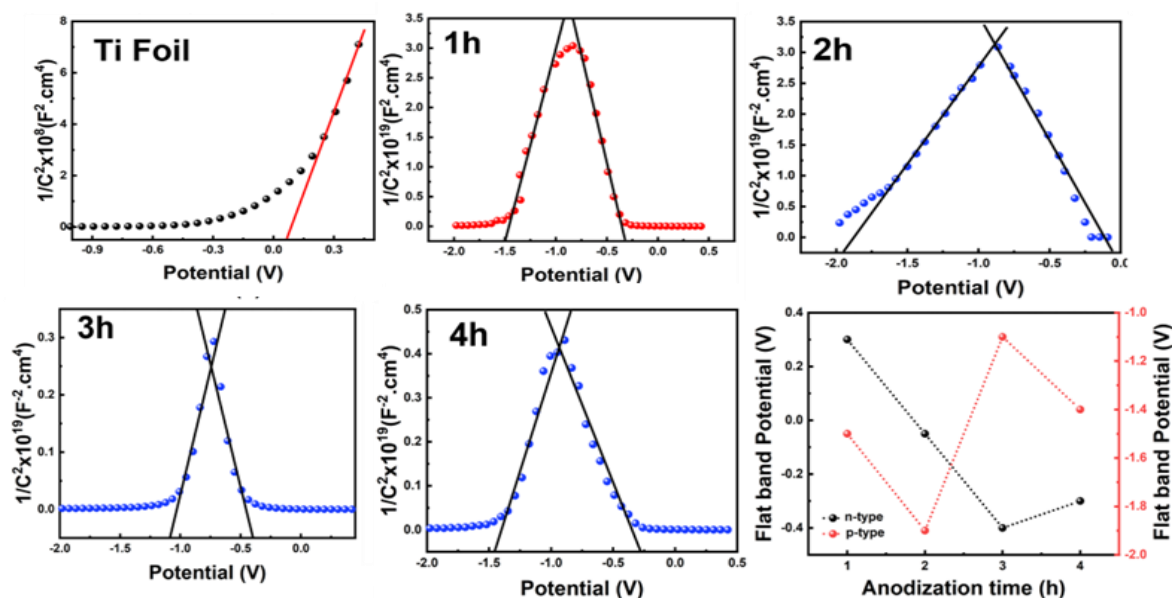


Figure 3, M-S plots for evaluating material type

XPS survey spectra were captured to study the surface chemistry and the chemical composition of as-prepared samples, as indicated in Figure 5. The XPS survey spectrum (Figure. 5a) clearly indicated that all the samples were mainly composed of elements Ti, O, C and F, whereas only the Ti sample contains N element. The presence of C, F and N in the XPS survey spectra might be ascribed to contamination.

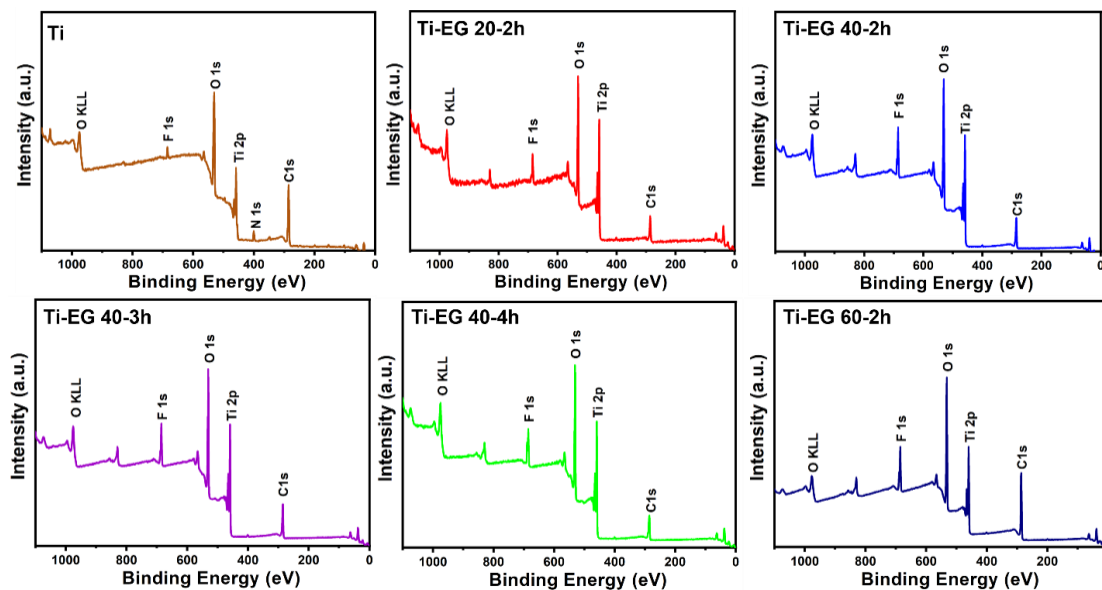


Figure 5a, XPS survey spectra to investigate the surface chemistry and chemical composition of samples (Ti, Ti-EG 20 at 2h, Ti-EG 40 at 2h, Ti-EG 40 3h, Ti-EG 40 4h, Ti-EG 60 at 2h)

Figure 5 b shows high-resolution XPS spectrum of Ti. In this spectrum, the Ti2p_{3/2} and Ti2p_{1/2} peaks can be deconvoluted into two sets of peaks, the stronger peaks at 459.5 eV and 465.2 eV correspond to Ti⁴⁺, confirming the main valence state in the as-prepared samples is Ti⁴⁺. A set of weaker peaks that appear at 457.7 eV and 462.5 eV can be attributed to the Ti³⁺ state. This might be due to the oxygen not being active enough to fully oxidize Ti, resulting in the formation of O vacancies and Ti³⁺ sites in TiO₂ lattice. Further, the energy separation between both Ti (2p_{3/2}) and Ti (2p_{1/2}) peaks is 5.7 eV reflecting the strong bonding between Ti and O atoms of the samples. As shown in Figure 1b, the small peak in Ti 2p high-resolution spectrum for the Ti sample located at 454.8 eV is associated with Ti-C bond. The Ti³⁺ species are produced via the Ti⁴⁺ reduction. To probe the oxygen vacancy (OV), we recorded oxygen core level spectra.

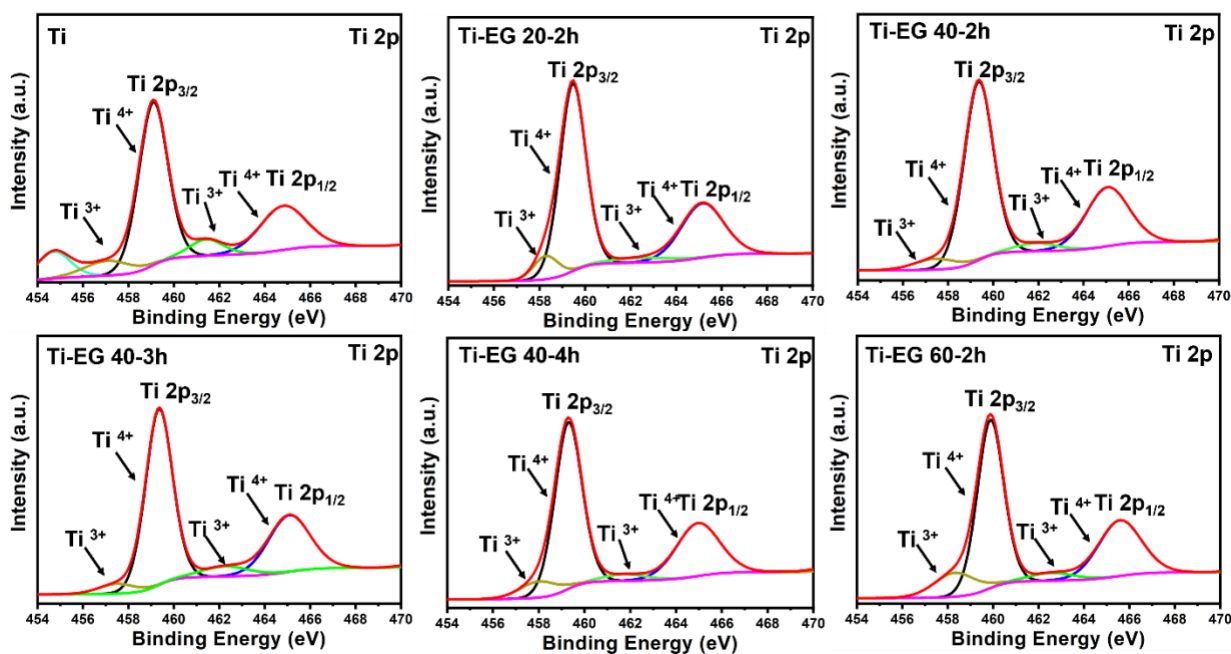


Figure 5b, high resolution XPS spectrum of Ti

Further, the high-resolution O1s XPS spectrum obtained for samples is shown in Figure 5c. The spectrum is fitted with three main peaks i.e., 530.3 eV, 531.8 eV, and 532.9 eV that correspond to

lattice oxygen of TiO_2 (Ti-O bond), and non-lattice oxygen. The peak at 531.8 eV is attributed to hydroxyl groups (Ti-OH) on the surface. The hydroxyl groups may be formed through the dissociation of surface-adsorbed water molecules obtained from the surrounding medium including aqueous solution and air moisture. After being heated, a significant decrease was noticed in Ti-OH's intensity whereas Ti-O's intensity was maintained, highlighting the significant role of hydroxyl groups to facilitate the formation of OV's on the surface of the samples. Furthermore, the high binding energy at 532.9 eV corresponds to surface contaminations of as-synthesized samples by adsorption of water molecules.

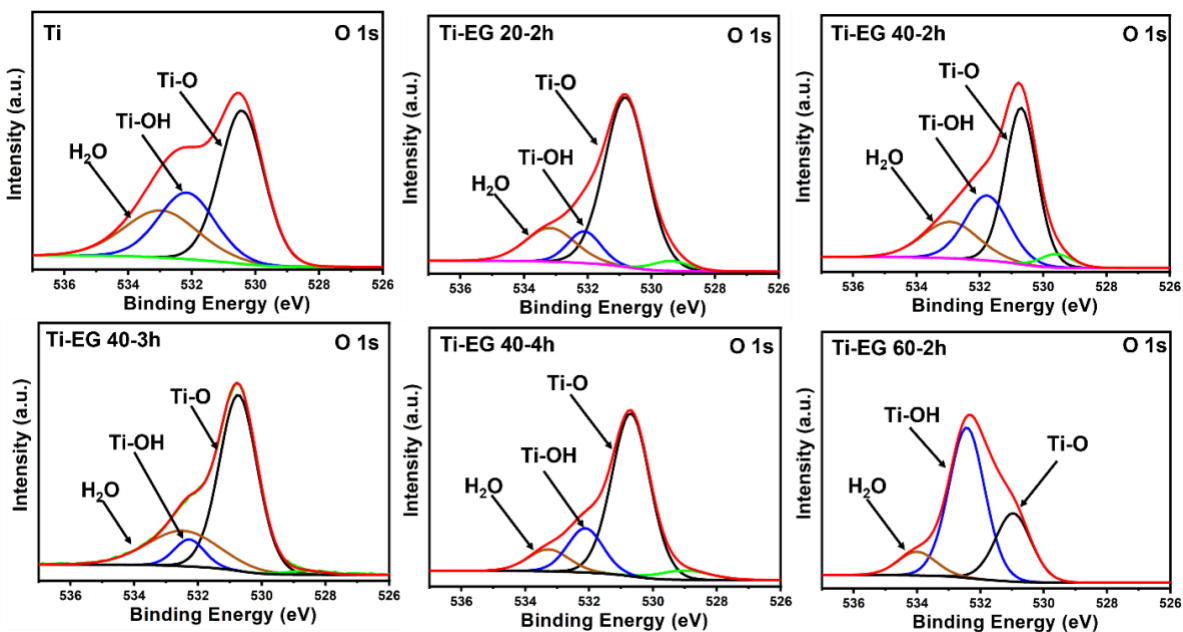


Figure 5c, O1s XPS spectrum

The occurrence of oxygen vacancy is consistent with the Ti^{3+} state as observed in Ti 2p core level XPS spectra. The observation of a very small peak at 529.3 eV is quite abnormal. The 529.4 eV bond energy component of O1s is associated with O_2^- ions found in oxygen-deficient regions within the TiO_2 matrix, promoted by the present chemical state of Ti^{3+} .

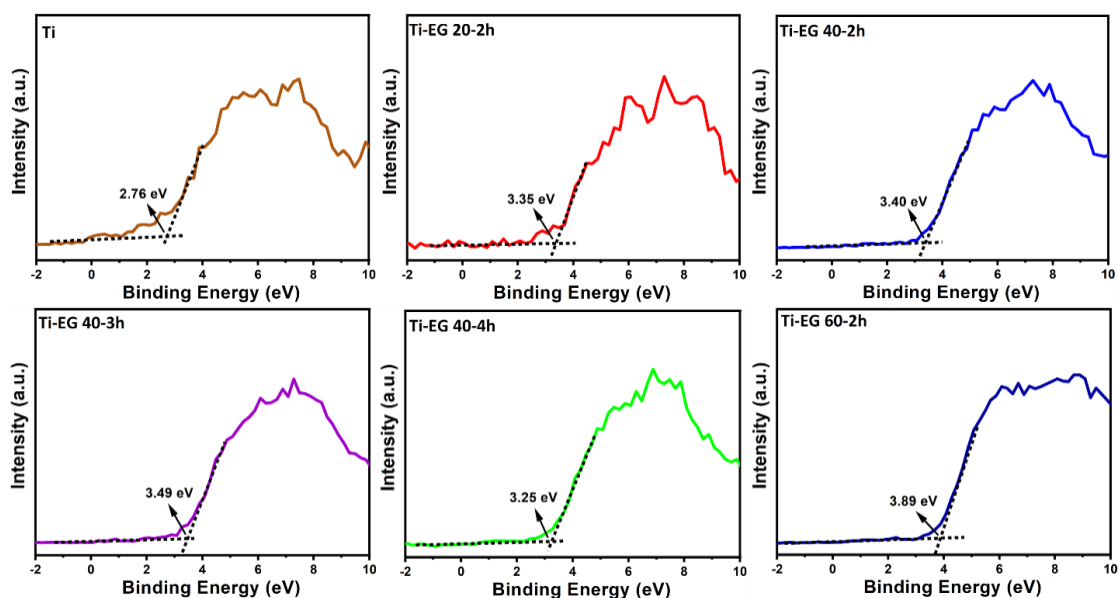


Figure 5d, XPS valence band region to highlight the VBM values

Furthermore, XPS valence band region spectra of as-prepared samples have been plotted in Figure 5d. The valence band maximum (VBM) of all samples has been obtained by extrapolating the leading edges of valence band spectra to the base lines. Observed VBM values are found to be 2.76, 3.35, 3.40, 3.49, 3.25 and 3.89 eV for Ti, Ti-EG 20-2h, Ti-EG 40-2h, Ti-EG 40-3h, Ti-EG 40-4h and Ti-EG 60-2h, respectively. To determine the actual VBM values, calibration with reference to the Fermi level should be done. Figure 6 illustrates the UV-VIS absorption spectra of TiO_2 -2h; it is clear from the figure that the material has strong absorption in the visible light and the UV region because it has two band gaps, (2.88 & 2.47) eV. From the XPS analysis we can assign this lowest band gap to defected Ti and/or oxygen vacancies.

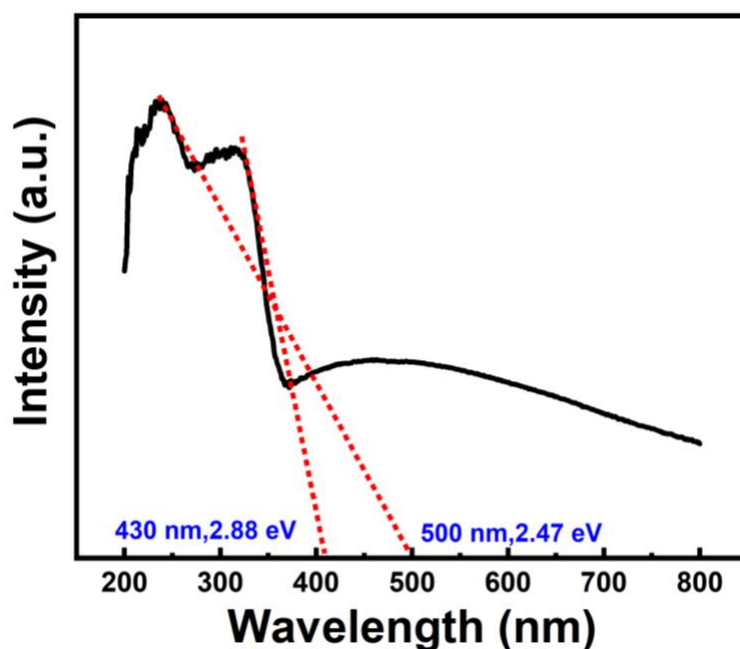


Figure 6, UV-VIS spectra to detect the band gap, best sample was detected which has 2 band gaps

To assess the photoelectrochemical performance a LSV was carried out in 1 M KOH inside photoelectrochemical cell with three electrode-configuration, to study the water oxidation and water reduction at dark and light conditions. Figure 2a, a series of LSV curves for all samples under dark for water oxidation and here the working electrodes were acted as anode, the sample Ti/TiO₂-2h stood out and had a higher current density (2.2 mA/cm²) at 1.23V vs RHE, while the lowest current at the same potential were (0.006 and 0.01 mA/cm²) for samples clean Ti foil and Ti/TiO₂/4h respectively, the reason behind the lowering the current could assign to the structure that form for oxidize the foil for long period time lead to form unformal oxide layer on the foil substrate and having large opened pores that might be trapped the bubbles and blocked some active site and thus hindered the water oxidation performance. Figure 7, it is the same experiment for above mentioned samples and again Ti/TiO₂-2h has greater current density (2.5) when exposed to the light. This little increased due to lowering the recombination rate and enhancing light harvesting. This will be proven later by XPS and UV-VIS spectroscopy.

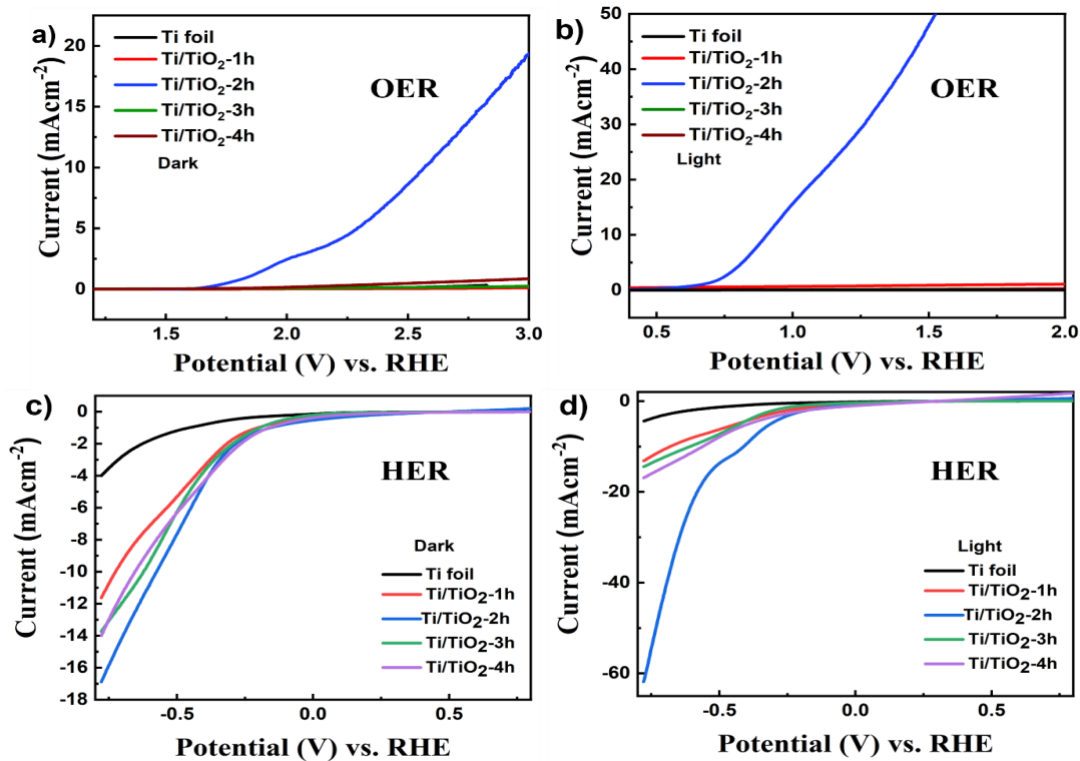


Figure 7 LSV illustrates the photocurrent tests for Ti foil and Ti/TiO₂ at different oxidation time for OER & HER.

Figure 8 illustrates Nyquist plots of Ti foil and Ti/TiO₂ between the time of 1-4h under dark and light condition. The semicircles represent the charge transfer resistance of the of Ti foil and Ti/TiO₂. As observed, the semicircular radiuses for (a) dark Ti/TiO₂ at 2h are smaller, which implies considerably lower charge transfer resistances. Indicating that figure (a) structure showed the best performance compared to under illumination which has a high charge transfer resistance due to higher photocurrent.

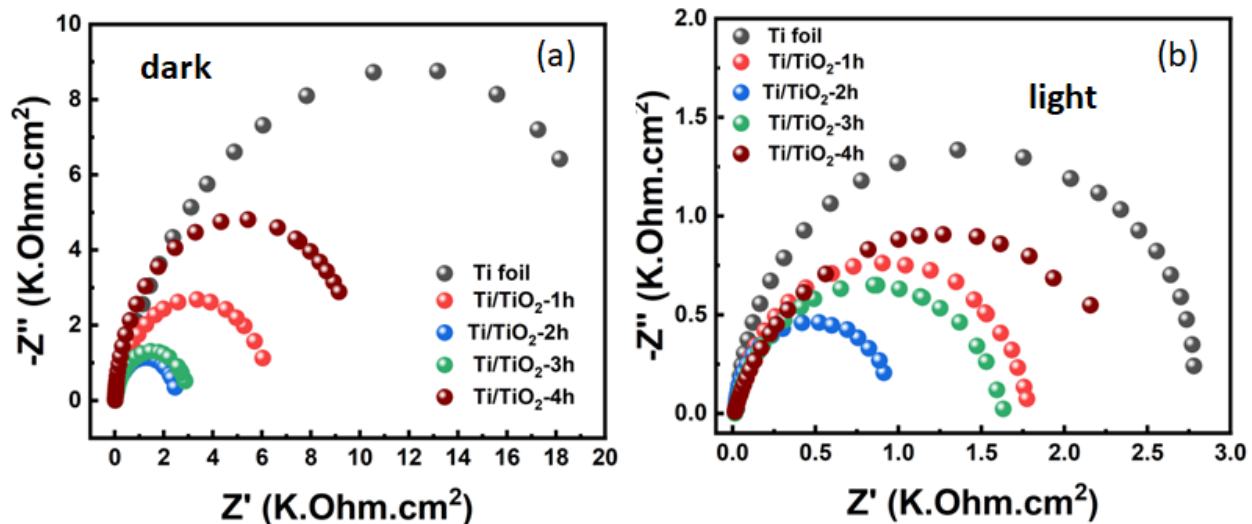


Figure 8: Nyquist plots for evaluating solution resistant R_s and charge transfer resistance

The stability test at figure 9 was characterized over 24 h to study the durability of the film under illumination condition for both reactions (OER & HER). The best sample showed a good and stable behavior over time, then LSV test was checked again after the stability test, no change in current or shift in potential had been recorded, which proven a perfect oxide layer has been formed.

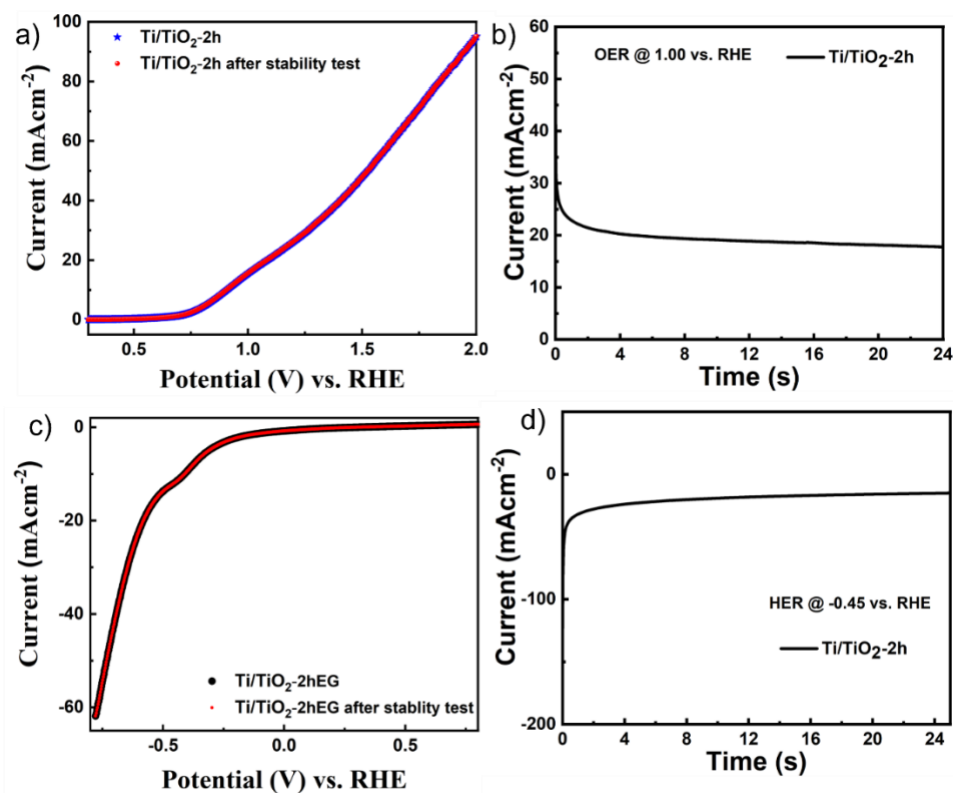
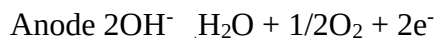
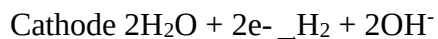


Figure 9, stability test to assess the durability under illumination conditions (OER & HER) of the Ti/TiO₂ before and after the stability test

Figure 10 shows the mechanism of splitting water for bifunctional Ti/TiO₂, when external voltage applied between two Ti/TiO₂ working electrode both OER and HER occurred at anode and cathode respectively in alkaline electrolyte of KOH



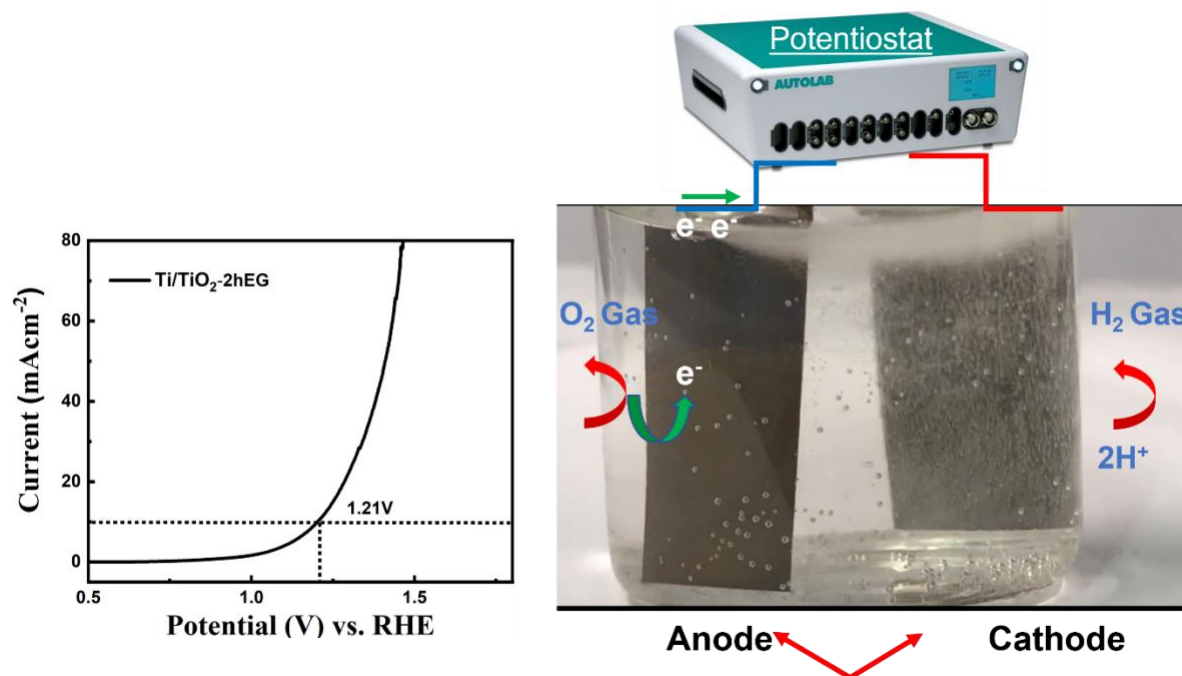


Figure 10, the water splitting mechanism for Bifunctional Ti/TiO₂

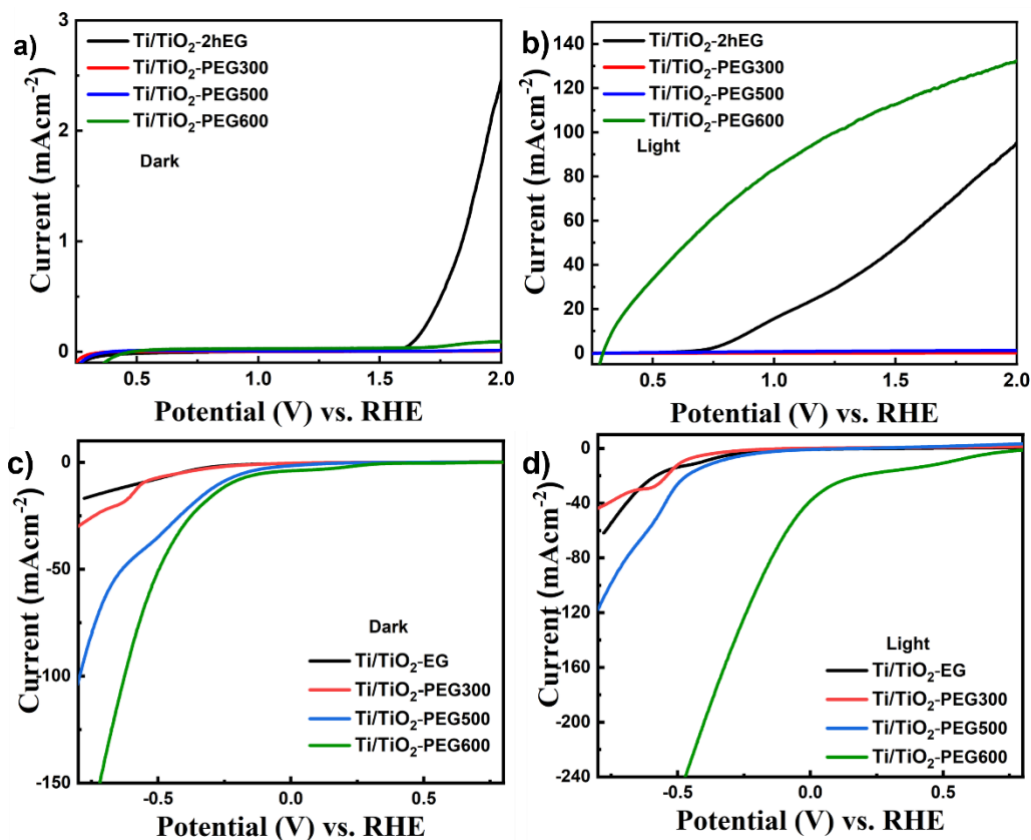
Conclusion:

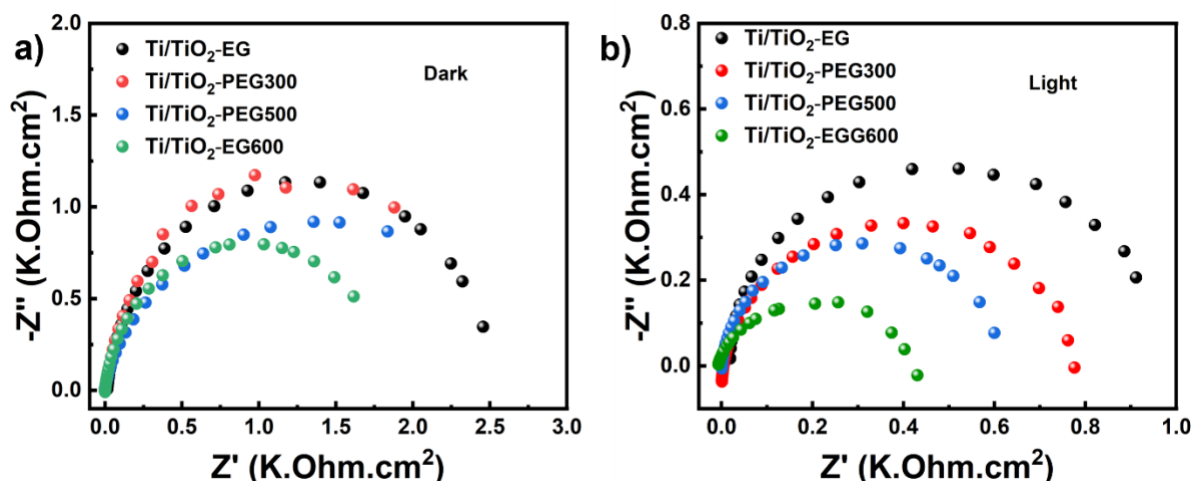
In the PEC water splitting field, researchers often focus on TiO₂ as photo anode only to separate Oxygen molecules. In this work, we demonstrated a study of enhancing 1 D TiO₂ film to perform as a bifunctional catalyst that works as both anode and cathode to split (both Oxygen and Hydrogen) by modifying the TiO₂ at different parameters like the anodic oxidation solution content, and anodic oxidation time to achieve the goal of getting the best results for hydrogen production.

Future work:

As mentioned before, one of the essential variables and parameters is the role of changing the EG chain to PEG with a different chain and molecular weight than the EG in the electrolyte solution. It plays a significant part in making clear pathways for the molecules and has made noticeable change. However, more investigation is needed study the impact EG to PEG has on the

morphology on Ti/TiO₂. Moreover, PL characterizations will be under consideration to prove the high performance of TiO₂ as cathode and overall water splitting under low voltage will be measured as well. Below some preliminary results of the effect of PEG on the morphology and water performance of TiO₂, it needs more analysis and extra experiments to draw a logic scientific mechanism.





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This study aims to demonstrate Ti Foil anodic oxidation as bifunctional nanostructured electrodes for water-splitting applications, addressing global energy demands. To advance this research, it is recommended to delve into the defect chemistry of titanium oxide, providing insights into the reduced energy bandgap resulting from the preparation method. Additionally, for practical testing, consideration should be given to the production rate of H₂ gas, and the use of a large-area electrode is essential for practical uses.