# Photocatalytic Separate Evolution of Hydrogen and Oxygen over Highly Ordered Nanorods and Bulk TiO<sub>2</sub> Thin Films

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Abstract—Three types of photocatalytic TiO<sub>2</sub> thin films with different structures, nanorods (NR-TiO<sub>2</sub>), mesoporous (MP-TiO<sub>2</sub>), and bulk structure (BK-TiO<sub>2</sub>), were prepared by evaporation induced self-assembling process or electron beam induced deposition method. The post-calcination treatment at 400°C was performed for all TiO<sub>2</sub> thin films to induce their crystallinity. The TiO<sub>2</sub> structure on the film properties were studied by material characterizations. The photoelectrochemical characteristics of the TiO<sub>2</sub> films were investigated using a potentiostat. Under UV-light irradiation, a highest net photocurrent of 0.747 mA was observed for the NR-TiO<sub>2</sub> thin film. To demonstrate the photoactivity of the prepared TiO<sub>2</sub> thin films, water-splitting reactions were conducted. The yields of hydrogen and oxygen were 35.8 and 17.2 µmole, respectively after 8 hr. of UV-light irradiation on NR-TiO<sub>2</sub>.

*Index Terms*—H-type reactor, nanorods, hydrogen, photocatalytic water splitting, renewable energy.

#### I. INTRODUCTION

Hydrogen is one of the promising solutions to the worsening crisis of global warming and energy shortage due to its advantages such as high energy yield, friendly to environment, and abundant in nature. The best way to produce hydrogen is to utilize sunlight to conduct the photocatalytic water-splitting reaction in the presence of photocatalysts. TiO<sub>2</sub> is a widely used photocatalyst because of its chemical stability, suitable band structure, and low cost. Honda and Fujishima in 1972 first reported the use of TiO<sub>2</sub> thin film as photocatalytic anode to split water into hydrogen and oxygen with the assist of bias voltage[1]. In order to improve the activity, to enhance the surface area of the photocatalyst has been developed [2]. In this regard, the use of nanostructured material can provide substantial surface area resulting in the enhancement of the photocatalytic hydrogen generation. Besides, the material with uni-directional electrical channels, e.g., nanorods and nanotubes, can increase the transfer efficiency of excited electrons.

Nanostructured  $TiO_2$  can be synthesized by various methods, such as anodic oxidation[3], spray pyrolysis[4], template sol-gel[5], hydrothermal[2], and evaporation induced self-assembling (EISA) process[6]. Among these methods, EISA process combines the advantages of sol-gel and hydrothermal methods. In this process, an ordered mesoporous  $TiO_2$  thin film is first prepared by using surfactants and the precursor of  $\text{TiO}_2$ . The mesoporous  $\text{TiO}_2$  thin film is then calcined in order to transform its mesoporous structure into crystalline nanopillars with inverse mesospace [7]. The nanopillar structured  $\text{TiO}_2$  thin film prepared by EISA method shows highly ordered orientation, perpendicular to the surface of the substrate. The crystalline nanopillars provide high porosity as well as surface area.

Over the years, nanostructured TiO<sub>2</sub> thin film has been investigated for the applications of dye-sensitized solar cell[3], organic pollutant removal[8], and gas sensor[9], etc. Recently, it has also been extensively used in water-splitting studies[10]. However, most of these studies rarely report the hydrogen yield obtained from an actual water-splitting reaction. In this study, we attempted to compare different TiO<sub>2</sub> thin films with nanorods, mesoporous, and bulk structures prepared by EISA process[7] and electron beam-induced deposition (EBID) [11], respectively, and their photocatalytic performances in carrying out the water-splitting reaction. Furthermore, the characterizations of thin films were carried out to reveal their crystallinity, surface morphology, chemical composition, etc. In order to clarify the photoactivities of the nanostructured TiO<sub>2</sub> thin films, photoelectrochemical measurement and water splitting reaction with separate hydrogen-oxygen generation in an H-type reactor were performed [12].

## II. EXPERIMENTAL

#### A. Preparation of $TiO_2$ Thin Films

Prior to the deposition of photocatalytic  $TiO_2$  thin films, Ti foil (0.127 mm thick, 99.7%) used as the substrate was cleaned with mixed aqueous solution (comprised of 33 wt% DI water, 33 wt% ethanol, and 33 wt% acetone) by ultra-sonic cleaner for 15 min, and then Ti foil was dried at ambient atmosphere and temperature.

Thin films of highly ordered  $\text{TiO}_2$  nanorods and mesoporous  $\text{TiO}_2$  were prepared by the EISA method reported by Wu et al.[7]. For the preparation of  $\text{TiO}_2$  nanorod thin film, 0.63 mL of 37 wt% hydrochloric acid (HCl) was drop wisely added into 1.05 g of titania tetraisopropoxide (TTIP) under vigorous stirring to perform hydroxylation. The hydrolyzed gel-like solution was mixed with 3 g of ethanol solution as well as 0.2 g of P123 (Pluronic P123, Block Copolymer Surfactant, BSAF). The mixture was spin-coated on the cleaned Ti foil at 500 rpm for 5 sec followed by 3000 rpm for 30 sec. The as-prepared TiO<sub>2</sub> was aged at -20°C for 1 day, and then heated to 400°C at a rate of 1°C /min and maintained at 400°C for 4 hr. The calcined TiO<sub>2</sub> thin film, referred to as NR-TiO<sub>2</sub>, exhibited the structure of highly

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ordered TiO2 nanorods.

The preparation procedure for mesoporous  $\text{TiO}_2$  thin film was similar to that for  $\text{TiO}_2$  nanorods as described previously. First, 0.522 mL of HCl was added drop-by-drop into 0.84 g of TTIP under stirring and further mixed with 3 g of ethanol and 0.15 g of F127 (Pluronic **(P)** F127, Block Copolymer Surfactant, BSAF). The mixture was spin-coated on cleaned Ti foil at 500 rpm for 5 sec followed by 5000 rpm for 30 sec. The as-prepared TiO<sub>2</sub> was aged at room temperature for 3 days and then calcined at 400°C under the same heating conditions as mentioned previously. The calcined TiO<sub>2</sub> thin film, referred to as MP-TiO<sub>2</sub>, revealed homogeneous mesoporosity on its surface.

Bulk TiO<sub>2</sub> thin film was prepared by EBID method[11]. Cleaned Ti foil was placed above the granular Ti<sub>3</sub>O<sub>5</sub> target (ADMAT MIDAS INC., grade 99.99%) in a vacuum chamber that was evacuated down to  $5 \times 10^{-6}$  torr as the base pressure. During deposition, O<sub>2</sub> (99.999%) was used as the reactive gas and the working pressure was  $8 \times 10^{-5}$  torr controlled by adjusting the O<sub>2</sub> injection flow rate. The TiO<sub>2</sub> thin film was deposited onto Ti foil by heating granular Ti<sub>3</sub>O<sub>5</sub> with an electron beam at 150°C. The deposited TiO<sub>2</sub> was calcined at 400°C for 4 hr under the same heating conditions as mentioned previously, and the sample was referred to as BK-TiO<sub>2</sub>.

## B. Characterization of TiO<sub>2</sub> Thin Films

The thickness of the TiO<sub>2</sub> thin films were determined mechanically by an Ambios Tech. XP-2 Stylus Profiler or observed from their cross-section SEM images. The crystallinity of prepared TiO<sub>2</sub> thin film was characterized by a Brucker-D8-ADVANCE X-ray diffractometer in the diffraction angle  $(2 \theta)$  between 20 and 80°, using Cu K $\alpha$ radiation as the source. To reveal the surface morphology of thin films, field emission scanning electron micrograph (FE-SEM) was carried out on a JEOL JSM-7600F without coating platinum or gold. The chemical composition of thin films was analyzed by OXFORD X-MAX80, energy dispersive spectrometer (EDS) incorporated with the FE-SEM. The UV-Vis absorption spectra of the thin films were measured by a diffusive reflectance UV-Vis spectrometer (Jasco V670) in the wavelength range between 300 and 800 nm. Specific surface areas of photocatalytic thin films were calculated by Brumauer-Emmett-Teller (BET) method. Before the adsorption measurement by Micrometrics ASAP2020/C5-05, the photocatalytic thin films were heated at 300°C to remove water vapor and then nitrogen was introduced as the adsorbate.

## C. Photoactivity of TiO<sub>2</sub> Thin Films

In order to determine the photoactivities of TiO<sub>2</sub> thin films, the photocurrent measurements were conducted by using a potentiostat, AUTOLAB PGSTAT302N, with a setup shown in Fig. 1 (a). Bias voltages between -0.5 and 1.5 V were employed at a scan rate of 0.05 V/s while dark current and photocurrent under UV light irradiation were recorded. The three-electrode cell comprised of the TiO<sub>2</sub>/Ti/IM (insulation material), Pt wire, and Ag/AgCl as the working, counter, and reference electrode, respectively. 1.0 M of KOH solution was used as the electrolyte. The working electrode (with area of 1 cm  $\times$  2 cm) was irradiated from the TiO<sub>2</sub> side by an UV light source produced from a 100-W Hg lamp (HL400EH-5 SEN LIGHT Corp.). The actual light intensity measured for UV (365nm) inside the reaction cell was  $3.2 \text{ mW/cm}^2$ .

For the photocatalytic water splitting, photoelectrodes were fabricated by coating a thin film of Pt on TiO<sub>2</sub>/Ti where TiO<sub>2</sub> was located on the opposite side of Ti. The prepared TiO<sub>2</sub>/Ti/Pt photoelectrode was assembled in the H-type reactor shown in Fig. 1(b). Afterward, 1 M of NaOH solution and 0.5 M of H<sub>2</sub>SO<sub>4</sub> solution were separately placed in a connected H-type reactor divided by a Nafion membrane (Nafion-117 Aldrich) and the TiO<sub>2</sub>/Ti/Pt photoelectrode. The TiO<sub>2</sub> and Pt side of the TiO<sub>2</sub>/Ti/Pt photoelectrode were in contact with NaOH and H<sub>2</sub>SO<sub>4</sub> solution, respectively. During the reaction, TiO<sub>2</sub> side of photoelectrodes was irradiated by UV light with an intensity of 25 mW/cm<sup>2</sup>. Gases produced from each chamber of the H-type reactor were collected by an on-line sampling loop (1 mL) and analyzed separately by a GC analyzer (China GC 2000), which was equipped with TCD (thermal conductive detector) and 3.5-m long molecular sieve 5A packed column to determine the concentration of gases.



Fig. 1. (a) Photocurrent measurement setup and (b) H-type reactor for water-splitting reaction

## III. RESULTS AND DISCUSSION

## A. Characterization of $TiO_2$ Thin Films

The morphological studies of TiO<sub>2</sub> thin films were conducted by SEM under 1,000x and 200,000x magnifications. Fig. 2(a) and 2(b) shows the SEM images of NR-TiO<sub>2</sub> and MP-TiO<sub>2</sub>, respectively, prepared by EISA method. The materials in gray are  $TiO_2$  while the spaces in-between  $TiO_2$  for NR-TiO<sub>2</sub> and MP-TiO<sub>2</sub> are the remaining P123 and F127 before calcination. After calcination, P123 and F127 were removed to form the inter-spaces or pores between TiO<sub>2</sub>, and nanorod or mesoporous structures were revealed. From Fig. 2 (a), the rod diameter of NR-TiO<sub>2</sub> is approximately 11-12 nm and the distance between rods is around 4-5 nm. On the other hand, the pore diameter of the MP-TiO<sub>2</sub> is 5-6 nm, slightly larger than the inter-rod distance of NR-TiO<sub>2</sub> as shown in Fig. 2 (b). Fig. 2 (a) also indicates that by using P123 as the template, mesoporous structure of MP-TiO2 was transformed into nanorods with inverse mesospace. However, by using F127, the original mesoporous structure of MP-TiO<sub>2</sub> was maintained. Furthermore, the thickness of NR-TiO2 and MP-TiO<sub>2</sub> is around 230 nm and 188 nm, respectively, observed from its cross-section SEM image (not shown). Fig. 2 (c) shows SEM images of BK-TiO<sub>2</sub>, indicating rather smooth surface morphology with only few cracks. Under higher magnification, definite crystal-like TiO<sub>2</sub> was observed on the surface of BK-TiO<sub>2</sub> thin film. The thickness of BK-TiO<sub>2</sub>, which is determined mechanically by a Stylus Profiler, could be well-controlled at around 200 nm by adjusting the experimental condition. Therefore, the thicknesses of BK-TiO<sub>2</sub>, NR-TiO<sub>2</sub> and MP-TiO<sub>2</sub> thin film are fixed at around 200 nm to eliminate the effect of thickness variation on thin film properties. From the BET analysis, the specific surface areas of NR-TiO<sub>2</sub>, MP-TiO<sub>2</sub> and BK-TiO<sub>2</sub> are 20.9, 16.4, and 9.1 cm<sup>2</sup>/cm<sup>2</sup> of substrate, respectively, indicating that NR-TiO<sub>2</sub> with manorods has higher surface area than MP-TiO<sub>2</sub> with mesoporous structures, and BK-TiO<sub>2</sub>. BK-TiO<sub>2</sub> shows the lowest surface area due to its relatively flat surface.



Fig. 2. SEM images of (a) NR-TiO2, (b) MP-TiO2, and (c) BK-TiO2 under 1,000x and 200,000x

Fig. 3 (a) shows the XRD patterns of NR-TiO<sub>2</sub>, MP-TiO<sub>2</sub>, and BK-TiO<sub>2</sub> thin films on Ti foil substrate (represented by TiO<sub>2</sub>/Ti). Compared with JCPDS-Power Diffraction File of Ti and TiO<sub>2</sub>, the XRD patterns of TiO<sub>2</sub> thin films were assigned mainly to the diffraction peaks of Ti and TiO<sub>2</sub>. Since the thickness of  $TiO_2$  (~200 nm) is much thinner than that of Ti foil (127 µm), TiO<sub>2</sub>/Ti exhibits mainly Ti signals, originating from Ti substrate. Even though Ti foil contributes most of the diffraction peaks, there are some anatase TiO<sub>2</sub> signals being observed, indicating the presence of crystalline TiO<sub>2</sub>. It is interesting to note that anatase TiO<sub>2</sub> signal of BK-TiO<sub>2</sub> is stronger than that of NR-TiO<sub>2</sub> and MP-TiO<sub>2</sub>. This is probably due to the denser structure of BK-TiO<sub>2</sub> and the fact that X-ray signals can penetrate deeper into the crystalline structure of TiO<sub>2</sub>. Since the signals for NR-TiO<sub>2</sub> and MP-TiO<sub>2</sub> are weak, XRD analysis of NR-TiO<sub>2</sub> and MP-TiO<sub>2</sub> on Si wafer was conducted. The XRD results of NR-TiO<sub>2</sub> and MP-TiO<sub>2</sub> on Si wafer are shown in Fig. 3 (b). Since the characteristic peak of Si (100) is at 69.13°, it will not interfere with the signals of TiO<sub>2</sub>. The crystal sizes of NR-TiO<sub>2</sub>, MP-TiO<sub>2</sub>, and BK-TiO<sub>2</sub> are 10.03, 8.41 and 34.78 nm, respectively as calculated from the Scherrer equation based on the broadening of XRD diffraction peak at around  $25.4^{\circ}$  which exhibits a preferential orientation of (101)[13].

Fig. 4 shows the UV-Vis absorption spectra of NR-TiO<sub>2</sub>, MP-TiO<sub>2</sub>, and BK-TiO<sub>2</sub> deposited on either silicon wafer or ITO glass. During the measurement, baseline was first carried out by using the substrate so that absorption solely from TiO<sub>2</sub> thin film can be obtained. Apparently, an absorption peak band at around 300-350 nm is observed for all three samples, which is attributed mainly to the absorption of TiO<sub>2</sub>. However, the intensity of the absorption peak for BK-TiO<sub>2</sub> is higher because BK-TiO<sub>2</sub> has denser TiO<sub>2</sub> film as compared with MP-TiO<sub>2</sub> and NR-TiO<sub>2</sub>. On the other hand, MP-TiO<sub>2</sub> and NR-TiO<sub>2</sub> have broadened absorption bands resulting from the scattering absorption induced by the porous structures. The UV-Vis spectrum of NR-TiO<sub>2</sub> shows a slight red shift in absorption relative to that of MP-TiO<sub>2</sub>, indicating that NR-TiO<sub>2</sub> could absorb a wider spectrum of sunlight for carrying out photoreaction.



Fig. 3. XRD patterns of (a) NR-TiO<sub>2</sub>, MP-TiO<sub>2</sub>, and BK-TiO<sub>2</sub> on Ti foil (b) NR-TiO<sub>2</sub> and MP-TiO<sub>2</sub> on Si wafer.



Fig. 4. UV-Vis absorption spectra of (a) NR-TiO\_2, (b) MP-TiO\_2, and (c)  $$BK\mathchar{BK}\mathchar{TiO}\mathchar{BK}\mathchar{TiO}\mathchar{Spectra}\mathc$ 

Moreover, the approximate band gap energy  $(E_g)$  of the material can be calculated from its UV-Vis absorption spectrum by using Eq. 1[14], where  $\lambda$  (nm) is the interception point of the extending tangent line of the material's characteristic peak with the wavelength axis of the absorption spectrum. The estimated band gaps of NR-TiO<sub>2</sub> and MP-TiO<sub>2</sub> are 3.40 and 3.45 eV, respectively, which are larger than that of BK-TiO<sub>2</sub> (3.20 eV) as well as the band gap of anatase TiO<sub>2</sub> reported in literature [14]. Usually, the band gap of semiconductor increases with the decrease of the particle size[15], which is consistent with the correlation

between band gap and crystal size obtained in this study: BK-TiO<sub>2</sub> (34.23 nm)  $3.20 \text{ eV} < \text{NR-TiO}_2$  (10.03 nm)  $3.40 \text{ eV} < \text{MP-TiO}_2$  (8.41 nm) 3.45 eV.

$$E_{g}(eV) = \frac{1240}{\lambda(nm)}$$
(1)

## B. Photoactivities of TiO<sub>2</sub> Thin Films

Fig. 5 (a) shows the cyclic voltammograms of NR-TiO<sub>2</sub>, MP-TiO<sub>2</sub>, and BK-TiO<sub>2</sub> under UV-light irradiation. Blank tests for the prepared TiO<sub>2</sub> thin films were also performed by carrying out the photocurrent measurements without light irradiation, which is referred to as dark current. Apparently, no dark current was observed at zero-bias voltage. On the other hand, significant photocurrent was observed under UV-light irradiation at zero bias for NR-TiO<sub>2</sub>, MP-TiO<sub>2</sub>, and BK-TiO<sub>2</sub>. Net current was calculated by subtracting dark current from photocurrent in order to predict the of the prepared photoactivity thin films toward water-splitting reaction. The net current of NR-TiO<sub>2</sub>, MP-TiO<sub>2</sub>, and BK-TiO<sub>2</sub> is 0.747, 0.530, and 0.675 mA, respectively. As expected, NR-TiO<sub>2</sub> shows the highest photocurrent generation due to its high surface area as well as the rod-like structure. In addition, NR-TiO<sub>2</sub> could absorb more light comparing with MP-TiO<sub>2</sub> as illustrated from the UV-Vis spectra, implying that more electron-hole pairs can be generated to conduct the water-splitting reaction. With higher surface area, more active sites of TiO<sub>2</sub> are in contact with the electrolyte, which is likely to enhance the yield for the water-splitting reaction. Moreover, the rod-like structure of NR-TiO<sub>2</sub> may facilitate electron transport due to the moving direction confinement, improving the separation of electrons and holes [16].

Hydrogen production via water-splitting reaction in an H-type reactor was carried out to demonstrate the photoactivity of the prepared TiO<sub>2</sub> photoelectrodes. As light irradiates on the TiO<sub>2</sub>/Ti/Pt photoelectrode, electron-hole pairs are generated on the surface of TiO<sub>2</sub> thin films. The electrons would transfer to Pt side through Ti foil to reduce hydrogen ions to hydrogen gas, while the holes on the  $TiO_2$ will conduct water oxidation to produce oxygen gas and hydrogen ions. As a result, separate evolution of H<sub>2</sub> and O<sub>2</sub> can be realized. This not only can prevent the possibility of an explosion for H<sub>2</sub>-O<sub>2</sub> gas mixture under high pressure, but also eliminate the cost of additional separation process for commercial application. The plot of the amount of hydrogen and oxygen evolved versus reaction time is shown in Fig. 5 (b). For NR-TiO<sub>2</sub>, the total amount of H<sub>2</sub> and O<sub>2</sub> evolved after 8 hr of UV-light irradiation is 35.8 µmole and 17.2 µmole, respectively, which is the best among the three types of  $TiO_2$ photoelectrodes prepared. As for the other two photoelectrodes, the total amount of H<sub>2</sub> and O<sub>2</sub> evolved is 18.9  $\mu$ mole (H<sub>2</sub>) and 9.7  $\mu$ mole (O<sub>2</sub>) for MP-TiO<sub>2</sub>, and 27.7 µmole (H<sub>2</sub>) and 10.9 µmole (O<sub>2</sub>) for BK-TiO<sub>2</sub> after 8 hr of UV irradiation. The yield of hydrogen obtained via water splitting has a positive correlation with the photocurrent generated. It is also noticed that the overall ratio of evolved  $H_2$  to  $O_2$  is consistent with the stoichiometric ratio (2:1) of hydrogen to oxygen in water.

Among these three photoelectrodes,  $NR-TiO_2$  shows the highest performance in hydrogen production due to its

nanorod-like surface morphology that possesses the highest surface area. With higher surface area, more TiO<sub>2</sub> active sites were in contact with the electrolyte solution to carry out the water-splitting reaction, resulting in higher photoactivity. In addition, different thin film morphologies may cause different boundary layers and concentration gradients on the film surface to further vary the performance of a photoelectrode. For instance, water can penetrate into the rod structure of NR-TiO<sub>2</sub> from all directions (x, y, and z-axis) while only uni-directional (z-axis) penetration could be achieved for MP-TiO<sub>2</sub> and BK-TiO<sub>2</sub>. It is expected that the penetration of water into the rod structure of NR-TiO<sub>2</sub> may reduce the concentration gradient of solution due to the decreased concentration barrier, meaning that more solution molecules will be available near the photocatalyst surface to perform the water-splitting reaction. As a result, higher photoactivity is observed for NR-TiO<sub>2</sub>. It is interesting to note that the photoactivity of BK-TiO<sub>2</sub> is higher than that of MP-TiO<sub>2</sub> despite the fact that BK-TiO<sub>2</sub> has lower surface area. This is possibly resulted from the higher crystallinity of  $TiO_2$  in BK-TiO\_2 (as shown in Fig. 5), which may also improve the performance of the photoelectrode by enhancing its charge transport property. Therefore, crystallinity and surface area are both important criteria of photocatalyst that may affect its performance. To sum up, TiO<sub>2</sub>/Ti/Pt with NR-TiO<sub>2</sub> thin film prepared by EISA method is proven to be an effective photoelectrode for carrying out the water-splitting reaction. The photoactivity of NR-TiO2 is the highest among other TiO<sub>2</sub> tested due to its nanorod structure that possesses the highest surface area, even though it has lower crystallinity as compared with BK-TiO<sub>2</sub>.



Fig. 5. (a) Cyclic voltammograms of TiO<sub>2</sub> thin films and (b)  $H_2$  and  $O_2$  yield vs. reaction time

#### IV. CONCLUSION

In this study, hydrogen production via photocatalytic water splitting was conducted by using TiO<sub>2</sub> thin films with different structures, such as NR-TiO<sub>2</sub>, MP-TiO<sub>2</sub>, and BK-TiO<sub>2</sub>. NR-TiO<sub>2</sub> and MP-TiO<sub>2</sub> were prepared by EISA process (a chemical method) and BK-TiO<sub>2</sub> was prepared by EBID (a physical method). After deposition, post calcination treatment at 400°C was performed for all TiO<sub>2</sub> thin films in order to form crystallized TiO<sub>2</sub>. A positive correlation between photocurrent and hydrogen yield from water splitting was observed for all TiO<sub>2</sub> thin films. Among these thin films, NR-TiO<sub>2</sub> shows the best performance in water-splitting reaction due to larger surface area and lower concentration gradient of solution. The comparison between BK-TiO<sub>2</sub> and MP-TiO<sub>2</sub> demonstrates that TiO<sub>2</sub> thin film with the higher crystallinity showed the better performance in both photocurrent and water splitting reaction. The overall ratio of generated hydrogen to oxygen for all three TiO<sub>2</sub> thin films is consistent with the stoichiometric ratio (2:1) of hydrogen to oxygen in water. By using NR-TiO<sub>2</sub> thin film as the TiO<sub>2</sub>/Ti/Pt photoelectrode, best performance in water splitting reaction was achieved to give hydrogen and oxygen yield of 35.8 and 17.2 µmole after 8 hr of UV irradiation, respectively.

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