Electrochemical synthesis of titania nanotube array for photoelectrochemical hydrogen production

Hidetaka Ishihara, Jacob P Bock, Rajesh Sharma Member, IEEE, Franklin Hardcastle, Alexandru S Biris, and Malay K Mazumder, Member, IEEE

Abstract—**Titanium dioxide (TiO_2) nanotube arrays have been extensively used during the last two decades for generating hydrogen by water photoelectrolysis and for many other applications involving photocatalysis, such as killing of bacteria, de-oderization, and gas sensors development. Several studies have reported the fabrication of nanotube arrays of different geometrical structures, with different length, inside diameter, and wall thickness. In this study, we report synthesis of TiO_2 photo-anodes with different nanotube geometries and the effect of the electrode surface structure on the generation of hydrogen. The nanotubular structures were produced by anodization and the tube structures were modified by varying anodization parameters such as electrolyte concentration, pH, voltage, and the time period of anodization. The surface of the nanotubular photo-anodes were then plasma treated with Helium (He) for removing contaminants and for reducing charge recombination sites followed by Nitrogen (N_2) plasma treatment for surface doping with N_2. The plasma surface treatment with N_2 was carried out for creating oxygen vacancies and for substitutional doping of N to treatment photo anodes bandgap at the surface. The results show that structural properties of nanotubular photoanodes and nitrogen plasma treatment have a significant effect on the photocurrent density.**

Index Terms—**Photovoltaic, Titanium dioxide, anodization, Photoelectrochemical cell, Water splitting.**

I. INTRODUCTION

Diminishing global energy resources and growing environmental concerns indicate that sustainable sources of energy will be in the future. Hydrogen is one of energy carriers for renewable energy; hydrogen economy has attracted extensive attention due to its environmentally clean character and recycling possibility [1]. Photoelectrochemical (PEC) generation of hydrogen using solar radiation for splitting water has several advantages for hydrogen generation: (1) Direct conversion of sunlight using semiconducting photoanodes for splitting water producing pure hydrogen, especially for fuel cell application (2) inexpensive and abundant availability of raw materials that is sunlight and water, (3) environmentally safe materials for large scale operation, and (4) relatively low capital and operating costs with no carbon foot prints. Yet the potential advantages of PEC technology for hydrogen generation have not been realized. In almost every PEC design, there are two major problems: (1) the bandgap of the semiconductor does not match the requirements in absorbing the visible spectrum of solar radiation and yet straddling electrochemical potential (1.23 eV) needed for splitting water, and (2) poor stability of the semiconductor photoanodes against the photocorrosion. Until now, no single semiconductor photoanode material has been found which satisfy both the critical requirements. TiO_2 electrodes meet the corrosion resistance requirements and its bandgap matches the need for electrochemical electrolysis of water but its large bandgap (3.2 eV) allows harvesting solar radiation only in the UV region, limiting its application. The photoelectrochemical properties of TiO_2 has generated significant interest following the pioneering work related to water photoelectrolysis by Honda and Fujishima [2,3]. In recent years, applications of TiO_2 for environmental cleanup such as destruction of organic compounds in polluted waters have been one of the most active areas in heterogeneous photocatalysis. However, the large bandgap of TiO_2 only allows photocatalysis using UV radiation, which comprises only about 7% of the solar spectrum [4]. Thus, reduction of band gap, creation of oxygen vacancies at the anode surface, and fabrication of TiO_2 nanotube array structure for (1) increasing the effective surface area and (2) reducing the charge carrier recombination rate are some of the key areas of current research for improving PEC based solar-to-hydrogen conversion efficiency [5-9].

Self-assembled vertically oriented TiO_2 nanotube arrays on Ti surface have been successfully produced by several authors [6-9] using anodization of titanium foil in a

H. Ishihara, J. P. Bock, and A.S. Biris are with the Department of applied Science, University of Arkansas at Little Rock, Little Rock, AR 72204, USA (e-mail: hxishihara@ualr.edu : jxbock@ualr.edu : asbiris@ualr.edu).

R. Sharma is with the Renewable energy technology program at Arkansas State University, USA (e-mail: rxsharma@gmail.com)

F.D. Hardcastle is with the Department of Physical Science, Arkansas Tech University, Russellville, AR 72801 USA. (e-mail: fhardcastle@atu.edu)

M.K.Mazumder, is with the Department of Electrical & computer Engineering, Boston University, Boston, MA, USA. (e-mail: mazumder@bu.edu)

fluoride-based electrochemical bath. The most remarkable properties of highly ordered nanotube arrays made by anodization of titanium are: (1) the effective surface area is increased many folds, (2) the diffusion of photogenerated holes across the wall of the nanotubes can be made efficient by making the wall thickness comparable to the diffusion length of the holes, (3) the electron mobility is improved since the conduction path is one-dimensional with minimal recombination loss as compared to the electron conduction in nanoparticles, and (4) the dimensions (length, wall thickness and internal diameter) of the nanotubes can be easily tuned to meet the specific needs. The tube length can be controlled by varying the anodization time, the diameter of the tubes are adjusted by changing the applied anodization voltage and the growth rate of the nanotubes is varied by ultrasonic excitation of the electrochemical bathe. Uniform titania nanotube array of various pore size (22-110nm), length (200-6000nm), outside diameter from 90 to 220 nm and wall thicknesses (7-34nm) have been reported [10] by tailoring electrochemical anodization conditions [4-11].

Several electrochemical processes have been used for the fabrication of nanotube arrays. For example, Zwilling et al [9] reported the formation of porous titania films in hydrofluoric acid (HF) or chromic acid electrolyte. Grimes and co-worker succeed in producing uniform 6.4 μm long titania nanotube arrays using a fluoride solution at pH 5.5. In 2007, they reported the anodic formation of a self-standing 134 μm long nanotubular arrays using ethylene glycol, NH_4F, and water electrolyte solution [5]. Raja and co-worker [7] reported the formation of nanotubular TiO_2 structure using phosphoric acid with hydrofluoric acid (HF) solution with ultrasonic excitation. The mechanisms of nanotubular formation during anodization process have been explained in several publications [5, 7, 9]. Recently we reported surface doping of nanotubular TiO_2 photoanodes using N_2 plasma [12]. In all of the previous studies, the nanotubular TiO_2 structures, when used as photoanodes, have shown significant enhancement photocurrent density and hydrogen production rate in photoelectrochemical splitting of water under simulated solar radiation. Clearly, optimization of the nanotubular array for maximizing both surface area and the surface structure for light trapping and surface doping to optimize the bandgap and band bending for absorbing light in the visible region are some of the most important topics of research on PEC based hydrogen production. In this paper we report the effects of variation of anodization parameters and plasma treatment process on the photoelectrochemical electrolysis of water. Effects of three successive stages of producing nanotubular TiO_2 structures, (1) anodization, (2) plasma surface treatments, and (3) annealing, on maximizing photocurrent density were studied.

II. EXPERIMENTAL

A. Anodization

Titanium (Ti) metal foils (99.7% purity) with thickness of 0.127 mm were purchased from Sigma-Aldrich and were cut into 18×18 mm^2 foils for anodization. Before electrochemical anodization, the Ti foils were degreased by ultrasonic treatments in acetone, ethanol, and deionized (DI) water successively for 5 min in each case. The Ti foils were then anodized in 0.5 wt % NH_4F (98% + ACS reagent, Sigma-Aldrich) in ethylene glycol (Anhydrous, 99.8%, Sigma Aldrich) with 0.2 % by vol DI water using ultrasonic bath (42kHZ, Cole Parmer 8890). Nanotubular TiO_2 arrays were formed by anodization using a two-electrode configuration with Ti foil as anode and a platinum electrode (thickness; 0.025 mm, 99.99% purity, area 3.75 cm^2, Sigma-Aldrich) served as a cathode. The separation between the two electrodes was kept at 1.0 cm in all the experiments. Anodization was carried out for different time periods at different voltages. In each case the voltage was held constant using a DC voltage supply (GW Instek, PSP-603) while anodization current was measured simultaneously along with the DC voltage applied using a computer. During anodization ultrasonic waves irradiated the electrolyte to enhance the mobility of the ions in the solution. The anodized samples were cleaned with distilled water to remove the occluded ions from the anodized solutions [9], and dried in a nitrogen gas. Table 1 shows the different conditions under which the nanotubular electrodes were produced.

B. Plasma treatment

The plasma reactor used for surface cleaning and doping consisted of two parallel aluminum electrodes across the plasma reactor. Plasma was generated between the electrodes using a 13.56 MHz RF power supply (MCS plasma Systems Model HF-3) with an impedance matching network. Samples were placed in a ceramic boat between the electrodes. The reactor consisted of a unique gas flow design where gas was dispersed in the chamber using a series of inlets from the top electrode [4]. Helium plasma was used to clean the electrode surface with an operating reactor pressure of 150 mTorr for 5 min. And after the surface cleaning, nitrogen plasma was used as processing gas at an operating pressure of 150 mTorr. Table 1 and 2 summarize the anodization, plasma treatment, and annealing processes used in the experiments.

C. Annealing

The anodized titania nanotubular arrays were annealed in O_2 atmosphere at 500°C for 2h to convert structure of the photoanode from amorphous to crystalline in the anatase form. The anodization process was carried out in two ways. In the experimental run # 1, all samples were annealed in oxygen atmosphere and in experimental run #2, the samples were first annealed in N_2 atmosphere followed by an annealing O_2 atmosphere. Before annealing, the samples were placed inside the annealing chamber which was purged with oxygen or nitrogen to remove air depending upon the annealing atmosphere to be used. Air purging was done with a gas flow rate of 200 sccm and during annealing the flow rate was

maintained at 50 sccm. The annealing temperature was adjusted to minimize the formation of rutile TiO_2 structure and maximize the anatase formation.

In the second set of experiments, the anodized titania nanotubular arrays were annealed in N_2 atmosphere at 600˚C for 2h to facilitate nitrogen doping. This was followed by passing heated O_2 gas through the samples and continued annealing in the oxygen atmosphere at 500˚C for 2h, with O_2 gas flow rate at 50 sccm.

TABLE 1
EXPERIMENTAL CONDITIONS OF ANODIZATION, PLASMA TREATMENTS AND ANNEALING IN EXPERIMENTAL RUN #1

Sample	Anodization Voltage and duration			Plasma treatment		Annealing
Sample 1	60V, 10min	40V, 10min	30V, 40min	He;5min	N₂;10min	O₂;500˚C,2h
Sample 2	60V for 60min			He;5min	N₂;10min	O₂;500˚C,2h
Sample 3	40V for 60min			He;5min	N₂;10min	O₂;500˚C,2h
Sample 4	20V for 60min			He;5min	N₂;10min	O₂;500˚C,2h
Sample 5	No anodization			No plasma		O₂;500˚C,2h

TABLE2
EXPERIMENTAL CONDITIONS OF ANODIZATION, PLASMA TREATMENTS AND ANNEALING IN EXPERIMENTAL RUN #2.

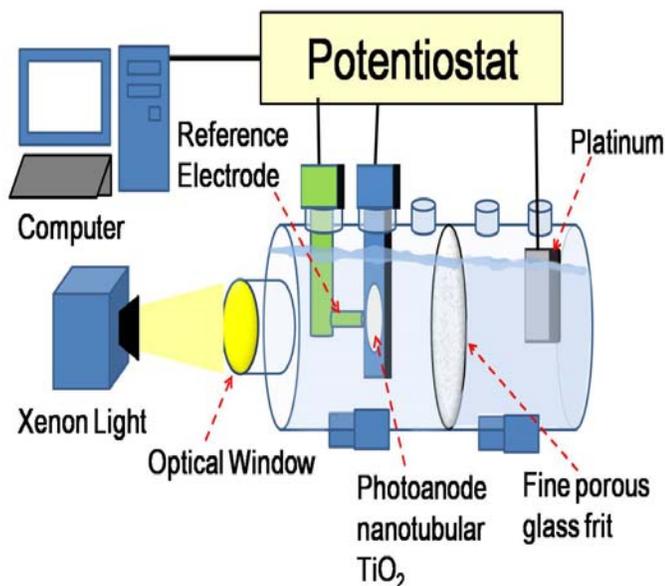| Sample	Anodization Voltage and duration	Plasma treatment		Annealing		
Sample2-1	20V for 60min	He;5min	N₂;10min	N₂;600˚C,2h	O₂;500˚C,2h
Sample2-2	20V for 60min	He;5min	N₂;20min	N₂;600˚C,2h	O₂;500˚C,2h
Sample2-3	20V for 60min	He;5min	N₂;60min	N₂;600˚C,2h	O₂;500˚C,2h
Sample2-4	20V for 60min	No Plasma		N₂;600˚C,2h	O₂;500˚C,2h

Fig.1. Experimental arrangement for measuring photocurrent density as a function of applied bias voltage with the photoanode samples exposed to simulated solar radiation at radiation intensity of 30 mW/cm^2.

D. Photoelectrochemical test of Photoanodes

Figure.1 shows the experimental setup for the photoelectrochemical (PEC) characterization of the samples. The PEC studies were carried out in a glass cell with separate compartments for photoanode (nanotubular TiO_2 electrode) and the cathode (platinum Foil). The compartments were connected by a fine porous glass frit. A reference electrode (Ag/Agcl was placed closer to the anode using a salt-bridge (saturated Kcl)-Luggin probe capillary. The electrolyte used was 1M KOH (pH ~14) aqueous solution. The electrolyte was prepared using regent grade chemicals and double distilled water. No aeration was carried out to purge out the dissolved gases in the electrolyte. The cell was provided with a 60 mm diameter quarts window for light incidence [2]. A 30mW Xenon lamp (ACRO light; HID) was used as light source. A potentiostat (EG&G instruments, Inc., Potentiostat/Galvanostat model 283) interfaced with a computer and software (PerkinElmer instruments, Inc., PowerSine) was used to control the potential and record the photocurrent. The samples were anodically polarized from the open circuit potential until 1.5 V at a scan-rate of 5 mVs^{-1} under illumination was achieved and the photocurrent was recorded.

III. RESULTS AND DISCUSSION

A. Current transient during anodization process

Fig.2a and 2b shows the current transient recorded during anodization of Ti at 20, 40 and 60 V for one hour. Fig. 2b shows the current transient for samples where anodization voltage was ramped from 60 to 20V. The current transient of samples anodized at constant voltage (Fig. 2a) exhibit similar behavior. Once the oxide layer is forward, the impedance between the electrodes increases, resulting in significantly reduced current between electrodes. Further, there is no change in impedance. The F ions cause field assisted desolation of Ti ions in solution. The three distinct current transient regions corresponding to applied voltages is evident in Fig.2b. But all of the three regions still demonstrate the same fundamental behavior as seen in Fig.2a.

B. Anodic polarization in 0.5wt% NH_4F+ethylene glycol with 2 wt% DI water

Fig.3 shows the SEM images of vertically aligned self-assembled nanotube arrays, anodized at three constant potentials: (1) 20V (Fig.2a), (2) 60V (Fig.2b), and (3) potential varied in three steps 60V-40V-20V (Fig.2c). At the constant potential of 20V, the sample showed combination of nanorods and dots structures. Nanotubes were not formed. The nanorods had average length of approximately 100 nm, and average diameter was 10 nm. The dots structures had the average 10 nm of square of side. The samples anodized at constant potential 60V had uniform nanotubular structure with a fairly uniform inside diameter of approximately 100 nm and an average center to center spacing of 150 nm, and the wall thickness was approximately 5 nm. The nanotube length was found to be approximately 4000 nm. The samples anodized at step voltages were expected to have shapes like cones as the anodization

voltage was reduced making the tube diameter smaller at the top. However, no significance difference in shape was observed compared to those structure obtained after constant voltage (60 V) anodization. To make appropriate shape analysis, it will be necessary to examine the bottom view of the nanotubes with a SEM. In the stepped voltage case, the bottom part of the tube array was anodized at 60V, and the mid layer anodization potential was 40V, and the top layer was formed at 20V. Additional anodization studies and high resolution shape characterization are needed to develop the desired conical structures of the nanotubes. The objective of the stepped voltage anodization was to separate tip of the tubes from one another to expose the tube walls to the incident radiation for trapping light.
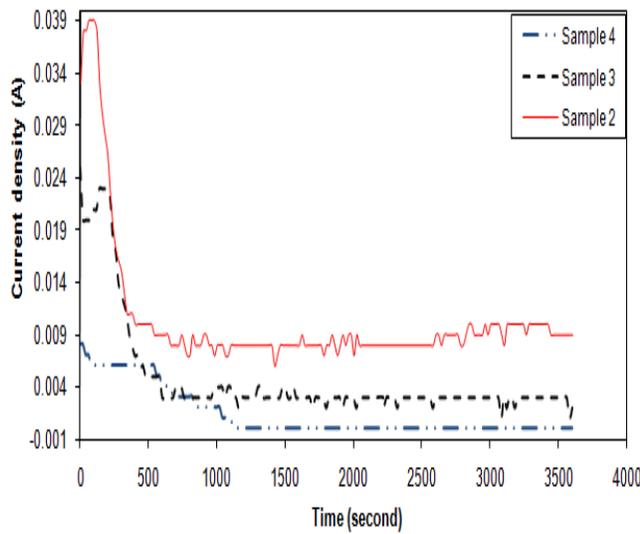
2a
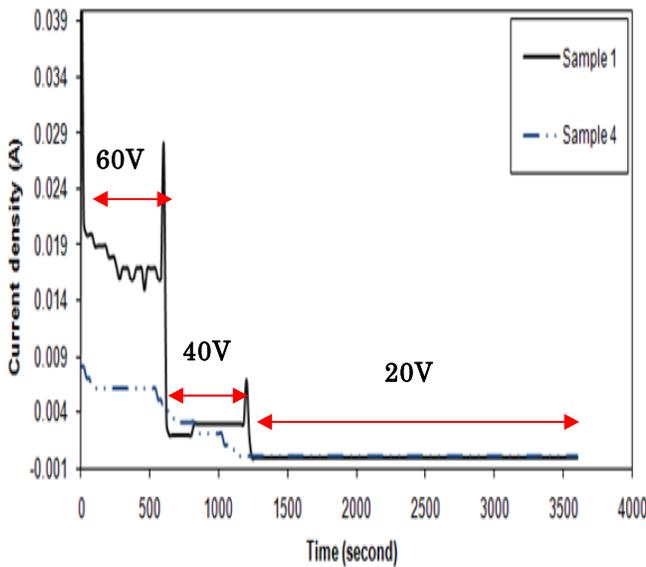
2b

Fig. 2 Current density vs time during anodization: (a) the different constant voltage anodization, (b) step voltage anodization at 60V-40V-20V compared with constant 20V anodization.
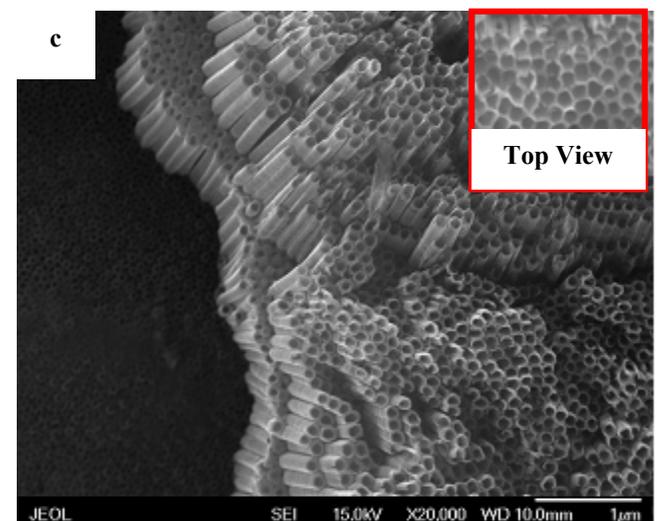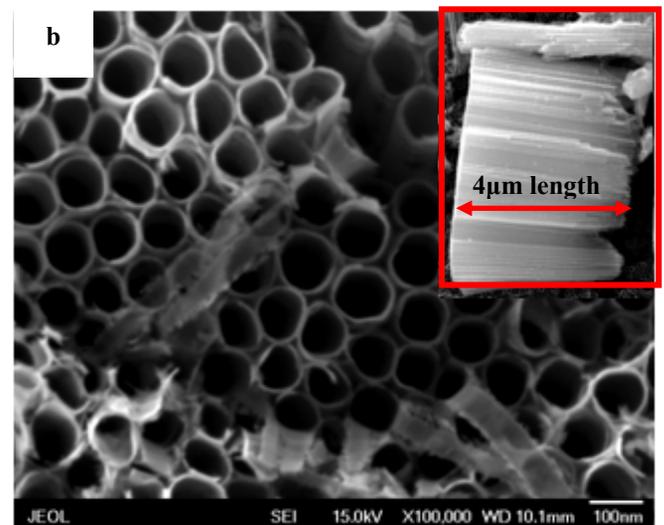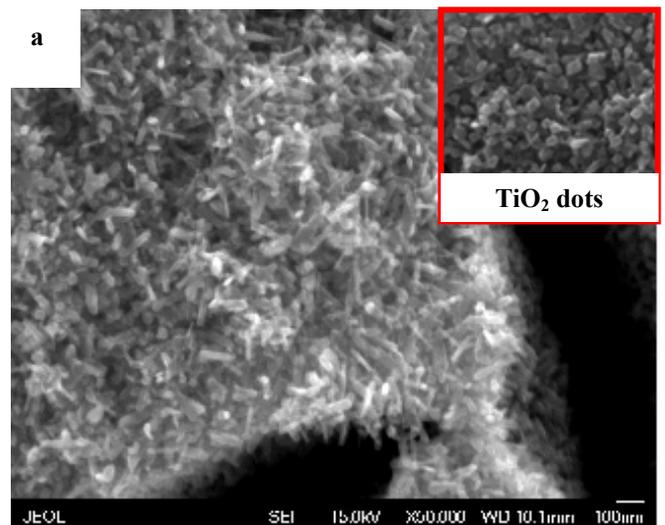

Fig.3 SEM image showing the TiO_2 sample anodized in a fluoride based electrolyte at three different voltage settings: (1) constant potential 20V (Fig.2a), (2) constant potential 60V (Fig.2b), and (3) stepped voltage potentials, 60V-40V-20V (Fig.2c)

C. *Photoelectrochemical characterization*

Fig.4 shows a comparison of the photocurrents density vs potential voltage for four anodized sample TiO_2 with Ti foil anode under Xenon lamp irradiation (30 mW/cm^2). At 0.7 V, the photocurrent density of the sample prepared by ramping the voltage during anodization was 55% greater than the value of the other constant voltage anodized samples. That the result agreed with the expected performance, stepped voltages in decreasing steps should produce nanotubular arrays of cone shaped tubes trapping incident light more efficiently compared to the case when the tubes are of uniform diameter and packed very closely to each other. Thus, the nanotubular geometry and N doping enhanced the photoelectrochemical performance of the sample compared to the others. In order to examine the variation of photocurrent density as a function of the duration of plasma treatment for N_2 doping on the surface of TiO_2 nanotubes, plasma treatment was carried out for different time periods: 10, 20, and 60 minutes. After the plasma treatment, each sample was annealed in N_2 atmosphere followed by O_2 annealing as shown in Table 2. In these tests, anodization of Ti foils was carried out at 20V for 60 min and one sample without any plasma treatment. Fig. 5 shows the photocurrents vs. bias voltage as measured for each of these samples after plasma treatment for different time period. From the plots, it is observed that the maximum photocurrent yield was obtained when the N doping by plasma was done for 20 min. Annealing of TiO_2 nanotubes at the optimum temperature and in the right gaseous atmosphere is also critical for obtaining maximum photocurrent density. Several studies have shown that annealing temperature in the range of 400 to 500° C is most effective in transforming the amorphous phase of TiO_2 to crystalline anatase form with minimal fraction in the rutile form. At a higher temperature, a more polycrystalline structure is formed with increasing amount of rutile structure.

Anodization in O_2 atmosphere is attributed to an increase in surface-absorbed oxygen causing an effective electron-hole separation [4, 10]. Physisorption of oxygen on the catalyst surface reacts with photogenerated electrons at the surface to form superoxide anion (O_2^-) radicals and hydrogen peroxide (H_2O_2) while the holes react with water to form hydroxyl radicals (OH*) thereby, preventing the recombination of photogenerated hole and electrons at the surface[4].

The photocatalysis reaction aided by physisorbed oxygen is advantageous in order to spatially separate the charge carriers created at the surface by the presence of both electron and hole traps. Beyond the surface and within the penetration depth of the photons, the charge separation occurs by space charge electric field and therefore, both the barrier height of the space charge region and crystalline anatase structure are needed for high electron mobility for the photogenerated electrons to reach the external circuit [4].

IV. CONCLUSIONS

The present work reports the importance of systematic investigations of (1) the geometric structure of the nanotube arrays, (2) the plasma process for surface doping of TiO_2 nanotubular photoanode with N_2 for decreasing surface bandgaps and (3) annealing process for crystallization for
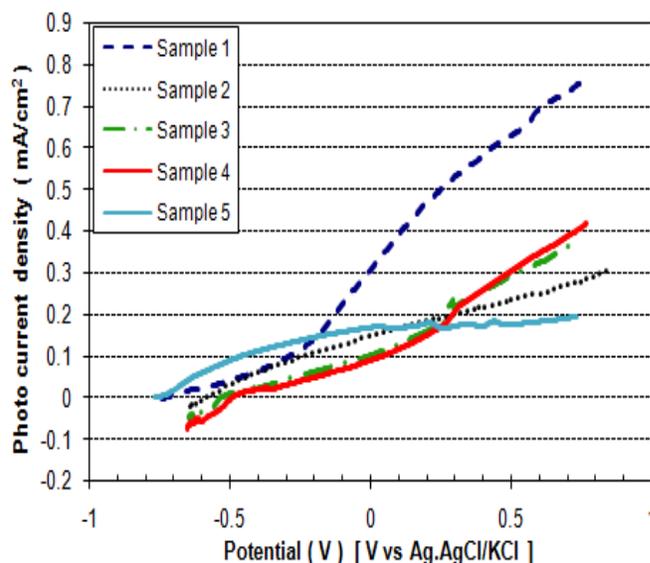

Fig.4 Photocurrent density vs bias voltage plotted for samples anodized at different voltages as shown in Table 1.
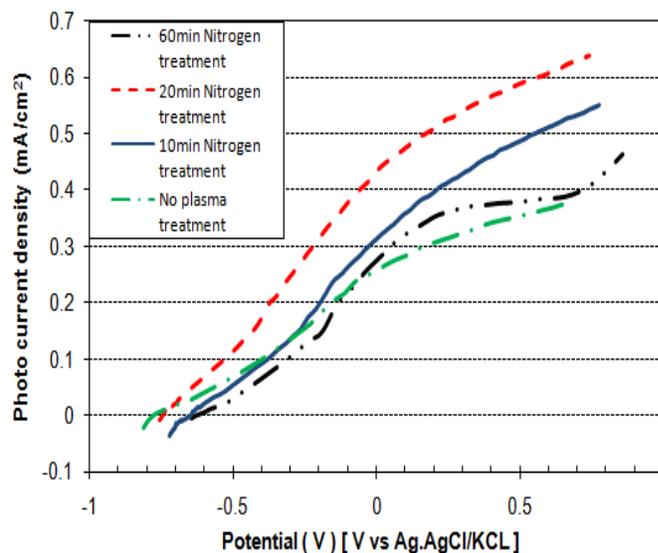

Fig.5. Photocurrent density vs. bias voltage plotted for anodized samples after plasma treatment for different time periods in nitrogen atmosphere. Anodization was performed at 20V for 60 min and all samples were annealed as shown in Table 2.

improving photocatalytic generation of hydrogen by splitting water. TiO_2 nanotubular photoanodes can be prepared by anodization of a titanium foil in an electrolyte containing ethylene glycol, ammonium fluoride, and distilled water.

The diameters of the nanotubes were varied by adjusting the anodization voltage and the length of the nanotubes were varied by varying the time period of anodization. In addition to the constant voltage anodization reported in many papers, conical shaped nanotubes with their bases larger than their tips were prepared by anodizing at stepped voltages 60V-40V-20V volts for a total time period of 60 min. Nanotubular structure of TiO_2 photoanodes prepared at stepped voltages showed 55% improved photocurrent density compared to the anodic structures prepared by constant voltage anodization.

The present studies also showed that plasma surface doping

in nitrogen atmosphere is very effective for improving photocurrent density. In sum, the test results show promising aspects of tuning several parameters involved in photoelectrochemical processes in improving conversion efficiency. The structural aspects and surface chemistry both influence greatly the efficiency of solar energy conversion in photocatalytic and photovoltaic processes.

REFERENCES

[1] L.Qiuey,"Significant Effect of pressure on the H_2 releasing from photothermal-Catalytic water steam splitting over $TiSi_2$ and Pt/TiO_2".2008, pp.376-379.

[2] A.Fujishima,"Nature". 1972, pp.238.

[3] A.Ghicov,"Annealing effects on the photoresponce of TiO2 nanotubes", Belmont, CA: Wadsworth, 1993, pp. 123–135.B. Smith, "An approach to graphs of linear forms (Unpublished work style)," unpublished.

[4] R.Sharma, P.P.Das, M.Misra, V.Mahajan, J.P.Bock. "Enhancement of the photoelectrochemical conversion efficiency of nanotubular TiO_2 photoanodes using nitrogen plasma assisted surface modification. Nanotechnology".Vol20.2009.pp.075704 (7pp)

[5] H.E.Prakasam, K.Shankar, C.A.Grimes," A New Benchmark for TiO_2 Nanotube array Growth by Anodization", J.Phys.Chem. C2007, 111, pp.7235-7241.

[6] G.K.Mor, O.K.Varghese, C.A.Grimes,"Areview on highly ordered, vertically oriented TiO_2 nanotube arrays: Fabrication, material properties, and solar energy applications", Solar Energy materials & Solar cells 90 (2006),pp. 2011-2075

[7] K.S.Raja,M.Misra,K.Paramguru,"Formation of self-ordered nano-tubelar structure of anodic oxide layer on titanium",Electrochimica Acta 51, (2005), pp.154-165.

[8] M.Kitano,K.funatsu,M.Anpo,"preparation of Nitrogen-substituted TiO_2 Thin Film Photocatalysts by the Radio Frequency Magnetron Sputtering Dposition Method and Their photocatalytic Reactivity under Visible Light Irradiation",J.Phys, Chem.B 2006,110,pp.25266-25272.

[9] S.K.Mohapatra, M.Misra, K.S.Raja."A novel method for the synthesis of titania nanotubes using sonoelectrochemical method and its application for photoelectrochemical splitting of water", J.catal, vol246, 2007, pp.362-369.

[10] J.C.Yu, J. Lin, D. Lo, and S.K. Lam,"Influence of thermal treatment on the adsorption of Oxygen and Photocataytic Activity of TiO_2", Langmuir, August, 2000,16(18), pp.7304-7308.

[11] A. Ghicov, S. P. Albu, R. Hahn, D. Kim, T. Stergiopoulos, J. Kunze, C.chiller, P. Falaras, and P. Schmuki, "TiO_2 Nanotubes in Dye-Sensitized Solar Cells: Critical Factors for the conversion efficiency", Chem. Asian J. 2009, 4, pp 520-525.

[12] R. Sharma,; Misra, M.; Mahajan, V.; Das, P. P., Bock, J.; Biris, A.S.; Mazumder, M. K., "Application of atmospheric-pressure plasma for enhancing photoelectrochemical properties of TiO_2 electrodes," *IEEE Industry Applications Society 43rd Annual Meeting*, Edmonton, Canada, 2008.