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Enhancing PEC Glucose Sensing of TiO_2 Nanotubes by Tuning the Length and Annealing Ambient

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Abstract. Self Organized and well aligned TiO_2 nanotube arrays (TNAs) has been synthesized by a simple low cost electrochemical method and applied as efficient photoelectrochemical glucose biosensor. XRD result revealed formation of TNAs all in anatase phase. Length of the tubes has been changed in the range of 0.6-3.9 μm, by varying anodization time from 0.5 to 4 hour to probe its effect on the biosensor performance. It has been found that although long tubes were more sensitive to low concentrations of glucose representing high photocurrent responses, nanotubes grown for 2 h was the optimum sample due to better mechanical stability and presenting more precise result. Moreover, annealing the optimum TNAs in Ar-H_2 caused more photoactive sample with nearly similar sensitivity against glucose. Hence, from energy level point of view, the formed oxygen vacancies did not participate in glucose oxidation reaction.

INTRODUCTION

From the first report on photocatalytic activity of a single-crystal TiO_2 electrode in water splitting reaction by Fujishima and Honda [1], extensive research has introduced titania as a promising catalyst due to its low cost, nontoxicity, unique structure, chemical inertness, remarkable properties and wide range of potential applications in degradation of organic pollutants, water-splitting, photovoltaic cells and other fields [2,3,4]. TiO_2 nanotube arrays have attracted increasing attention due to offering large surface area compared to nanoparticles and reasonable transport properties leading to enhancement in photoelectrical and electrochemical performances.

Glucose sensors have raised considerable interest over the past few decades due to the emergence of diabetes mellitus as a worldwide public health challenge. Clark and Lyons [5] utilized glucose oxidase to fabricate the first enzyme electrode in 1962 and then, scientists have developed different types of glucose enzyme sensors. Although Enzymatic glucose sensors present desired selectivity and sensitivity in practical applications, they suffer from their instability, complex enzyme immobilization, and high sensitivity to temperature, pH, and humidity. To overcome these drawbacks, non-enzymatic amperometric glucose sensors has been proposed by scientists [6,7].

The principle of an amperometric glucose sensor is generation of electrons in catalyst-assisted glucose oxidation [8], resulting in a measurable current response with a linear behavior versus glucose concentration. In another approach, named as photoelectrochemical (PEC) biosensing, a nanostructure semiconductor acts as a photocatalyst and the photorespons current density will be recorded as a result of glucose oxidation reaction on the surface initiated by photoexcited charge carriers [9,10].

Herein, TiO_2 nanotube arrays have been fabricated by anodizing method with variety of tube lengths to find their optimum thickness in PEC glucose biosensing. Moreover, the effect of oxygen vacancy in TNAs structure on its sensing performance has been studied by annealing the optimum sample in reducing gas ($Ar+H_2$).

EXPERIMENTAL METHOD

TNAs Preparation

Self-organized TiO_2 nanotubes arrays were fabricated based on a conventional anodization method which is reported before [11]. First, titanium sheets (99.5% purity, 0.5 mm thickness) were anodized in an electrolyte solution containing deionized (DI) water and ethylene glycol with a ratio of 10:90 with 0.1 M NH_4F. Small amount of 1M H_3PO_4 was used for adjusting pH at 5.6. The anodization was performed at 60 V for 30, 60, 120 and 240 min. After the anodization, samples were sonicated for about 30 s in pure DI water to eliminate the depress surface layer and open the nanotube's mouth. Then, the all layers were heated with the rate of 1.5 ^oC/min and annealed at 520 ^oC for 6 h to complete crystalline formation. Moreover, to scan the effect of oxygen vacancies in the anatase lattice, samples anodized for 2 hours also h ours also heat treated at 400^oC under flow of $Ar+H_2$ (80%-20%).

Characterization

Crystalline structure of the samples was studied by x-ray diffraction (XRD) spectroscopy (Cu source, PEN analytical). All morphologies were investigated based on scanning electron microscopy (SEM, TESCAN-VEGA3-SB). To measure PEC glucose detection level, photoresponses were recorded in a three electrode glassy reactor using Ag/AgCl, Pt and TNAs as reference, counter and working electrode, respectively. The reactor was equipped with a quartz window putting the photoanodes behind it and illuminating the layer by UV-A (λ = 368 nm, SYLVANIA,20 W). Linear sweep voltammetry (LSV), cyclic voltammetry (CV) and chronoamperometry (CHA) measurements were performed by galvanostat/potentiostat system (Autolab, model 302). All scan rates were selected 100 mV/ and reported potentials were versus the Ag/AgCl reference electrode. In all experiments, 0.1 M of aqueous $NaNO_3$ solution was used as electrolyte.

RESULTS

Crystalline Structure

Figure. 1 shows XRD pattern of TNAs layer anodized for 2h. It is clear that all observed peaks were attributed to the grown layer with no detected impurity in the crystalline lattice. The main peak at $2\theta = 25.3o$ was related to anatase phase in (101) orientation and some other peaks was attributed to Ti substrate. It can be concluded that stoichiometric TiO2 was formed in pure anatase phase. Similar results were observed for TNAs synthesized for 0.5, 1 and 4 hours.

Surface Morphology

Figure. 2. Shows SEM images of the all fabricated nanotubes from top and side view. Based on Fig. 2a for the sample anodized for 2 h, average diameter and wall thickness of 150 and 60 nm, respectively. According to the results, anodization time did not change the surface morphology of tubes and just caused to form longer tubes for longer time. Accordingly, the thickness of photoanodes (length of the tubes) was obtained 0.6, 1.4, 2.7 and 3.9 μm for the samples anodized for 0.5, 1, 2 and 4 hours, respectively keeping the integrity of the whole layer.

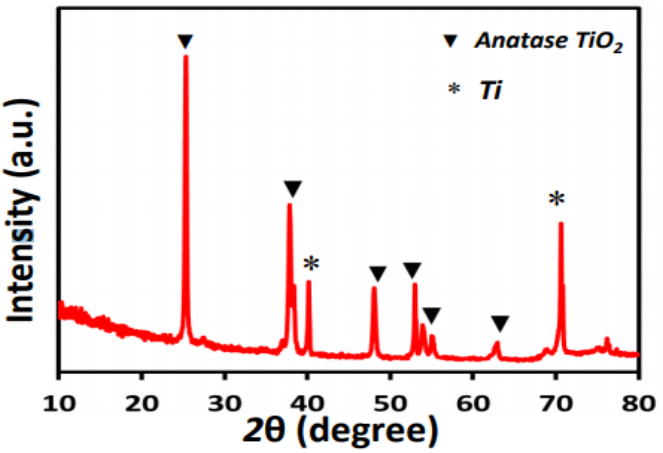

Figure 1. XRD pattern of TNAs grown for 2 h.

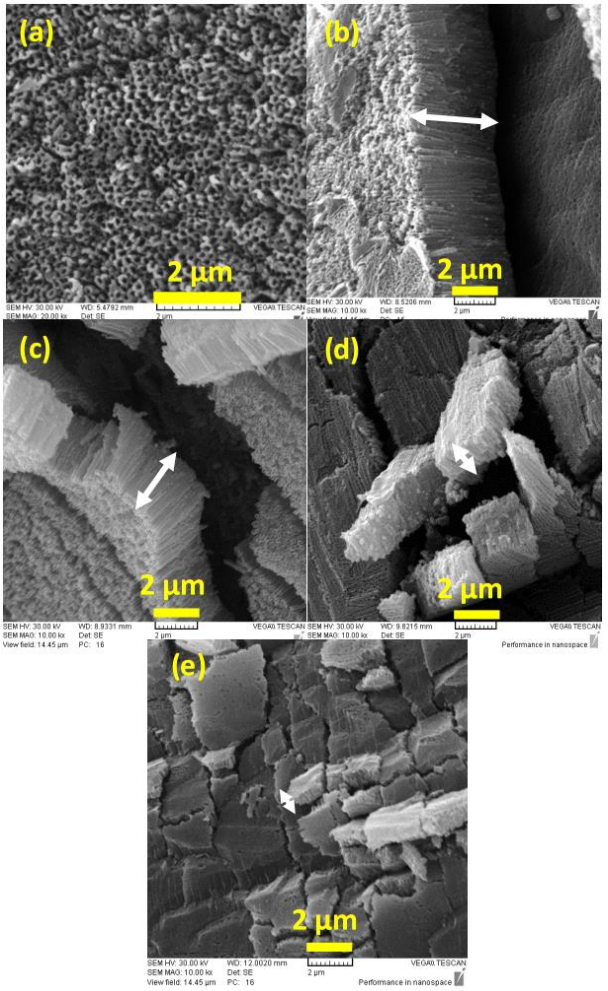

Figure 2. SEM morphology. (a) top view image of TNAs grown for 2 h and Cross-sectional view of TNAs grown for (b) 4h, (c) 2h, (d) 1h and (e) 0.5h

Photoelectrochemical Glucose Sensing

First, to scan photoresponse of TNAs in the UV-A irradiation at various applied biases, LSV technique was used in 0-1.2 V window potential as illustrated in Fig. 3a. It can be seen that for the all samples, photocurrent of the nanostructures increased by increasing the applied anodic bias as a result of more favorable water oxidation on the surface. However, the maximum value of photocurrent density was achieved at 1.2 V equal to 52, 62, 66 and 69 $\mu A/cm^2$ for the samples anodized for 0.5, 1, 2 and 4 hours, respectively. Hence, longer tubes led to higher photocurrent due to more photoactive material on the surface and more light harvesting effect. This result indicated that despite of some reports [12] stated lower efficiency for longer tubes due to defects and difficulties in electron transport, in our systems, the positive effect of thickening TiO_2 layer was dominant.

On the other hand, it is obvious that annealing the sample in $Ar+H_2$ ambient leads to higher photocurrent due to well know oxygen vacancies formed in the layer which caused more photo activity of TNAs. In addition, for the later sample, photocurrent reached to saturated value (~ 80 $\mu A/cm^2$) at lower applied anodic bias due to newly formed band bending at electrode/electrolyte interface.

To study performance of TNAs in PEC glucose biosensing, photocurrent of the samples was recorded versus time at +0.5 V under chopping condition in different steps each contained specific concentration of glucose in the electrolyte. To this purpose, I-t graphs were first recorded without glucose (#1) while in the second step (#2) glucose concentration was increased to 0.02 mM. This process was continued until saturation condition occurred as typically presented in Fig. 3b for the sample anodized for 2 hours. In fact, the observed increase in the photocurrent by the increase of glucose content in the electrolyte reflected TNASPEC biosensing performance even at very low concentrations of the analyte. The observed saturation could be due to surface passivation of TNAs as a result of adsorbing glucose oxidation byproducts on it as also reported elsewhere [13]. Additionally, photocurrent of the all samples in step #1 have been listed in Table 1.

Figure. 3.c presents dependence of TNAs photoresponse on the glucose concentration for all samples which is characteristic of a PEC biosensor. For all fabricated samples, by increasing glucose concentration from very low value (0.02 mM), at first, photorespose of the sensor increased with a nearly linear manner while it approached to a saturation value at higher concentrations. This behavior introduced a sloped for linear part, α (μA/mM.cm^2) as sensitivity factor of the PEC biosensor and a specific glucose concentration, Co (mM) which is the higher detection limit of the sensor. These obtained quantities extracted from Fig. 3c have been listed for the all samples in Table 1. It is clear that by increasing TNAs length, the both α and Co values increased significantly suggesting longer anodization times as more efficient PEC biosensors. To probe how the results are accurate and precise, experiments for each growth conditions have been repeated several times using duplicates of each sample and the obtained uncertainty for each parameter has been also included in table 1. It is obvious that although long times (4 h) resulted higher values for sensing parameter and saturation limit, their standard deviation in both these parameters were also higher the ones for the other samples. This result would be a consequence of low mechanical stability and undesired attachment of these long tubes to the

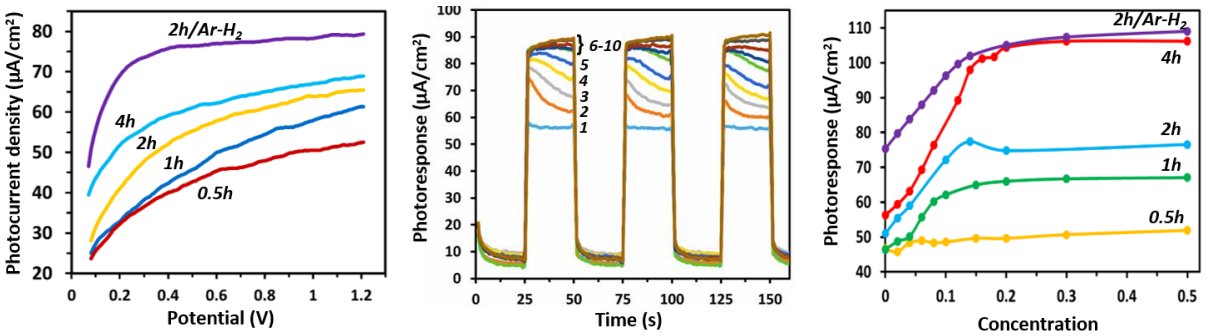

Figure 3. (a)linear sweep voltammetry and (c) photoresponse versus concentration of TNAs for different growth condition and annealing ambient (b)choronoamperometry curve of TNAs for 2h growth condition with different concentration of glucose (numbers 1-10 are related to 0, 0.02, 0.04, 0.06, 0.08, 0.10, 0.12, 0.15, 0.20, 0.30 and 0.50 mM glucose concentration respectively)

TABLE 1

T(h)	I_{ph} (μA)	α (μA/mM.cm^2)	C_0(mM)
0.50	46.1±0.6	55.0±15.5	0.04±0.00
1	43.5±8.6	145.4±32.8	0.12±0.03
2	53.7±3.7	244.5±48.0	0.14±0.01
4	57.9±1.1	255.5±62.9	0.18±0.01
2 / Ar-H_2	72.9±1.7	188.4±8.7	0.018±0.02

substrate leading to detachment from Ti back contact during synthesis and/or ultrasonic step. This uncontrolled

changes in these layers caused high standard deviations in the samples confining their application as practical PEC glucose sensor. Considering these positive and negative aspects, the sample anodized for 2 hours has been suggested as the optimum ones with sensitivity of about 244.5 ± 48.0 μA/mM.cm^2 with 0.14±0.01 mM saturation concentration.

Based on Fig. 3 c and table 1, annealing this sample in reducing ambient caused to higher photocurrent density in the absence of glucose as mentioned before. However, it did not show positive effect on the sample sensitivity which means that the formed oxygen vacancies and their correspondence energy levels did not participate in glucose oxidation reaction on the TNAs surface.

CONCLUSION

In summary, TNAs photoanodes have been fabricated by anodizing method with different lengths and applied as PEC glucose biosensore. Using XRD and SEM analysis, formation of anatase crystalline phase as well as tubular morphology have been confirmed. All photocurrent densities in the absent of analyte and photoresponses against various concentrations of glucose have been studied systematically introducing 2 hours and annealing in air as the optimum growth and annealing conditions, respectively, leading to 244.5 ± 48.0 μA/mM.cm^2 as sensitivity factor and conditions 0.14 ± 0.01 mM as upper performance limit for glucose concentration. This result suggests the grown TNAs as a promising semiconductor host for future modifications.

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