STUDY ON EFFECT OF MORPHOLOGY AND CRYSTALLIZATION OF TIO_2 NANOTUBES AND SPECTRAL DEPENDENT IPCE (%) OF TIO_2 NANOTUBES IN AQUEOUS SOLUTION

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Abstract

The formation of TiO_2 nanotubes arrays were investigated in different electrolyte solutions. Three nanomaterials of TiO_2 were prepared by electrochemical anodization using three different electrolyte solutions:0.5 wt.% NH_4F with 4 wt.%, 6 wt.%, and 8wt.% of distilled water in ethylene glycol. SEM showed different morphologies caused by the variation in the water content of the solutions. By a change of the crystalline phase of the TiO_2 nanotubes, the oxygen vacancies increased and affected to the optical and electrical properties of TiO_2 nanotubes. To understand the interplay between the photoactivity and light absorption of TiO_2 nanotubes annealed at 300℃, incident-photon-to-current-efficiency of TiO_2 nanotubes was investigated as the function of the wavelength of incident light. IPCE% is a better parameter reflecting the spectral dependent photon response of TiO_2 nanotubes.

Keywords: Anodization, TiO_2 nanotube arrays, IPCE% of TiO_2 nanotubes

Introduction

Global warming is an aspect of climate change, referring to the long-term rise of the planet's temperatures. It is caused by increased concentrations of greenhouse gases in the atmosphere, mainly from human activities such as burning fossil fuels and farming. There are three positions on global warming: (1) that global warming is not occurring and so neither is climate change; (2) that global warming and climate change are occurring, but these are natural, cyclic events unrelated to human activity; and (3) that global warming is occurring as a result primarily of human activity and so climate change is also the result of human activity.

The current global economy is largely dependent on fossil fuels. Because of the depleting reserves and the gross environmental impact of burning fossil fuels, the identification of suitable alternative and renewable energy sources, such as hydrogen, is becoming increasingly important.

Hydrogen gas is foreseen as the future energy carrier since it is renewable and does not generate the greenhouse gas carbon dioxide in combustion.

Due to global warming, artificial changes in seasons and droughts occur. As a result, extreme temperatures, extreme cold, drought, floods, irregular rainfall, and lighting are occurring. Among these things, the greenhouse effect is caused by high temperatures and carbon dioxide. Carbon dioxide gases were detected using sensitive devices. In doing so, gas sensors are very useful for gas detection. Therefore, the properties of TiO_2 nanotubes, which are commonly used in gas sensing.

Titanium dioxide (TiO_2) is a semiconductor material that can form nanostructures and produce valuable optical and electrical properties. TiO_2 has been used in a range of industrial and consumer products. TiO_2 can be tailed into various shapes, such as nanoparticles, nanorods, nanowires, and nanotubes. Due to each tube’s growth array on the surface, nanotubes have attracted the most attention among these nanostructures. The titanium dioxide nanotube arrays

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have a unique nanoarchitecture, a large surface area, and higher mechanical stability than TiO_2 nanoparticles [3].

TiO_2 nanotubes can be synthesized using different types of methods, such as electrochemical anodization, the template-assisted method, and hydrothermal. Electrochemical anodization is an electrolytic technique capable of increasing the oxide layer thickness. Anodization is a facile practical approach due to its highly ordered and vertically oriented nature. All favorable properties render TiO_2 nanotubes suitable for various applications such as photocatalysis, sensors, and dye-sensitized solar cells.

Generally, the TiO_2 nanotubes require heat treatment at high temperatures to sustain crystallization. Therefore, the fabrication of TiO_2-based sensor properties could certainly promote multifunctional sensitivity behavior and high-efficiency applications that may lead to newer opportunities in disciplines as diverse as physics, chemistry, biology, medicine, and engineering. Due to the metal oxide-based semiconductor produced at a lower cost with higher productivity and performance, TiO_2 film can be used in domestic, industrial, electronics, semiconductors, refineries, metal, or other furnaces [15].

The recorded anodization current against time curves suggests that the high current density shows high chemical dissolution occurs when radicals are present in the electrolyte during anodization, which speeds up the formation of long TiO_2 nanotube arrays. Therefore, the morphology of TiO_2 nanotubes could be optimized by the proper varying water contents.

In this period, surface morphology, the crystalline phase, and photocurrent density of different TiO_2 nanotubes (4 wt.% H_2O, 6 wt.% H_2O, and 8 wt.% H_2O) were investigated. In this research work, TiO_2 nanotube arrays were fabricated by the anodization method. The changes in structure and dimension of TiO_2 nanotubes were investigated by varying the water content in the electrolyte.

Materials and Method

In the present investigation, TiO_2 nanotubes were created on pure titanium surfaces through the anodizing method using an electrolyte solution with varying water contents in the electrolyte solution. Titanium foil (thickness: 0.2 mm; purity: 99.7%) was cut into 2cm x 2cm pieces, which were ultrasonically cleaned for 5 minutes each in acetone and ethanol, then rinsed in distilled water. The samples were dried by using a hair dryer. The samples require a very efficient cleaning procedure in order to obtain an almost perfect, fine surface. Then samples were immersed into the electrochemical cell with the electrolyte solution, which is mainly based on hydrofluoric solutions or an organic solution. In order to study the variation of water contents, the experiments were performed by varying the water contents in the electrolyte by 4wt.%, 6 wt.%, and 8 wt.% of distilled water, whereas ethylene glycol is 96wt.%, 94 wt.%, and 92 wt.%. This composition of electrolyte solution was stirred for 30 minutes with a magnetic stirrer before anodizing.

Anodization was performed in a standard two-electrode electrochemical cell with Ti foil as the working electrode and a platinum rod (diameter: 1mm, purity: 99.9%) as the counter electrode connected to a DC power supply. When the DC power supply was applied between two electrodes, gas bubbles were observed at the platinum rod during anodization. The anodization was performed at room temperature under magnetic stirring. The applied voltage between the titanium sample and the platinum rod was 30 V, and the anodization time was 1 hour. The voltage was gradually increased to 30 V. The distance between titanium foil and cathode was

kept constant at 2 cm for every experiment. The as-prepared samples were ultrasonically cleaned with acetone for 1 minutes, rinsed in distilled water, and then dried in air for characterization.

Characterization

The morphologies and sizes of the TiO_2 nanotubes were investigated by Scanning Electron Microscope SEM (Phenom World, MVE 0356841799, ε00-07334). In the standard high vacuum (HV) operating mode, the MVE 0356841799 is capable of operating in extended pressure mode (EP). The MVE 0356841799 SEM operates with acceleration voltage. The elemental composition as atomic percentage (At %) of oxygen, titanium, and fluorine were measured by energy dispersive X-ray spectroscopy at 10 keV (EDS). Nanotubes were studied by X-ray diffraction using a Bruker D8 powder diffractometer operating in the reflection mode with Cu Kα radiation (40 kV, 30 mA) diffracted beam monochromator. (Cu-Kα radiation, $\lambda = 1.5406$ nm) starting from 0.2 to 15 kV and can attain magnification up to 135, 000 X. X-ray diffraction (XRD) is a versatile, non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of the sample.

Potentiostatic Voltammetry

Photoelectrochemical (PEC) properties of TiO_2 nanotubes were investigated using the CS350 electrochemical workstation. The linear sweep photoelectrochemical measurements were done in a standard three-electrode system containing TiO_2 nanotubes as the working electrode, a Pt rod as the counter electrode, and Ag/AgCl as the reference electrode. The photocurrent density measurements were done using a 1M KOH solution with the addition of 1 wt.% of ethylene glycol in both the dark and light irradiation conditions. Linear sweep photovoltammetry was obtained with a scan rate of 0.05 V/s in a potential window of -1 V to +1 V. 100 W LED light sources with different wavelengths (Red 665 nm, Yellow 590 nm, Green 515 nm, and UV 370 nm) were used as the light sources.

Results and Discussion

TiO_2 nanotubes were grown in electrolyte solution with varying water content concentrations. In order to look for an optimal concentration of water content in electrolyte, we have studied the dependence of morphology and size of TiO_2 nanotube arrays on the water contents in electrolyte solution. Figure(1)(a), (b), and (c) show SEM images of TiO_2 nanotubes prepared from the electrolyte solution with water contents of 4 wt.%, 6 wt.%, and 8 wt.%.

In the SEM image of water content of 4 wt.% figure(1(a)), nanotubes were formed at the most parts of the sample. The amount of water (4 wt.%) and the amount of ammonium fluoride (0.5 wt.%) in electrolyte are in equilibrium state for nanotubes formation. It was found that the sizes of the nanotubes are homogeneous in larger areas. The circular diameter well defined. It was found small ripples and sponges in the nanotubes. The size distribution histogram figure (2(a)) indicates that the diameter of nanotubes ranges from 20 nm to 75 nm with maximum frequency of size 45 nm-50 nm. The amount of water (4 wt.%) and the amount of ammonium fluoride (0.5 wt.%) are at optimum condition.

In the SEM image of water content of 6 wt.% figure(1(b)), the circular diameter well defined. It was found a lot of ripples and sponges in the nanotubes. The size distribution histogram figure(2(b)) indicates that the diameter of nanotubes ranges from 40 nm to 85 nm with maximum frequency of size 55 nm-60 nm.

In the SEM image of water content of 8 wt.% figure (1(c)), the circular diameter well defined. It was found a lot of ripples and sponges in the nanotubes. The size distribution histogram figure (2(c)) indicates that the diameter of nanotubes ranges from 35 nm to 85 nm with maximum frequency of size 50 nm-55 nm.

As we can see, different morphologies were obtained, the wall thickness increases, and both the inner diameter and the control in the concentration of water in the electrolyte solutions increase. Therefore, the nanotubes trend to form random packets without a particular shape on the top of nanotube arrays. On the contrary, a low concentration of water (4 wt.%, 6 wt.% and 8 wt.%) promotes self-organization and self-ordering of the TiO_2 nanostructures, causing the wall thickness to be thinner and the circular diameter well defined. Thereby, the nanotubes synthesized with 4 wt. % and 6 wt.% (H_2O distilled) obtained a better ordering and organization than the nanotubes synthesized with 8 wt.% content of water in electrolyte solution.

Additionally, Table 1 shows the elemental composition of the TiO_2 films on the titanium substrate after electrochemical anodization. For all samples, the ratio between Ti and O is similar, however, the TiO_2 films closest to their stoichiometry are the samples 4 wt % and 6 wt % films with the lowest contents of water because they have approximated ratio of 1:2, 1:1.97 ($Ti \leq O_x$), these ratios are attributed to titanium substrate and complete oxidation. Therefore, these can be seen that the films contain elements of the electrolyte solution such as F, O etc.

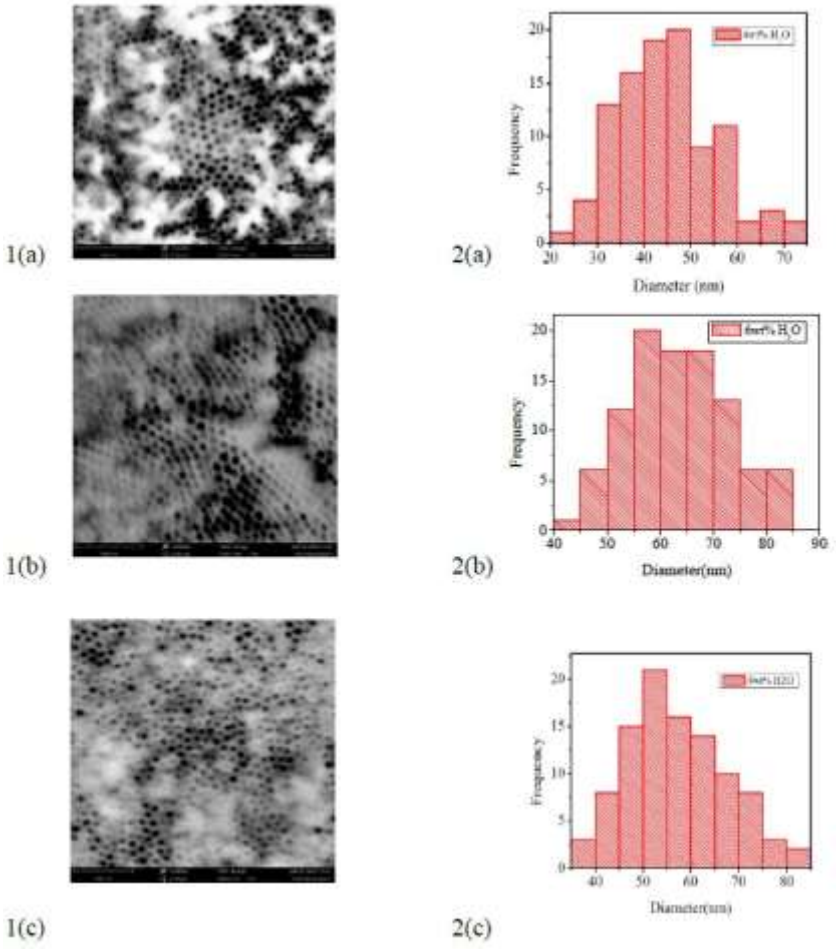

Figure1(a-c) SEM images of titanium nanotube sample obtained at 30V for anodization time of 1hr.

Figure2(a-c) Size distribution histogram for TiO_2 nanotubes prepared from electrolyte solution with varying water content.

Table 1. elemental composition of the TiO_2 nanotubes prepared by eletrochemical anodization

Sample Name	Water content in lectrolyte solution	O At %	Ti At %	F At %
Sample 1 (4 wt % H_2O)	4 wt %	58.96 ± 1.55	27.62 ± 0.31	13.43 ±0.77
Sample 2 (6 wt % H_2O)	6 wt %	59.69 ±1.45	30.31 ± 0.30	10.01 ± 0.61
Sample 3 (8 wt % H_2O)	8 wt %	59.04 ±1.42	31.91 ± 0.30	9.06 ± 0.58

For the crystalline phase of TiO_2 nanotubes, an XRD study was carried out. Figure 3 shows the XRD patterns of TiO_2 nanotubes annealed at 300 °C. After thermal treatment 300 °C, the amorphous structure is converted to the anatase crystalline phase. The typical peaks were observed at 25.5, 38.5, 40.5, 48.8, 53.2, and 63.2, corresponding to the planes (101), (103), (112), (200), (105) and (213), respectively. Anatase phase is a crystalline structure used in gas sensing since it presents better chemical and structural stability and higher catalytic activity than other structures of TiO_2 (rutile and brookite). It was seen that the crystallized sizes of TiO_2 nanotubes decrease as the temperature increases with varying water content in the electrolyte solution. Among the anatase annealed at 300 ℃ , the largest peak intensity is found in the 6 wt.% and 4 wt % H_2O samples.

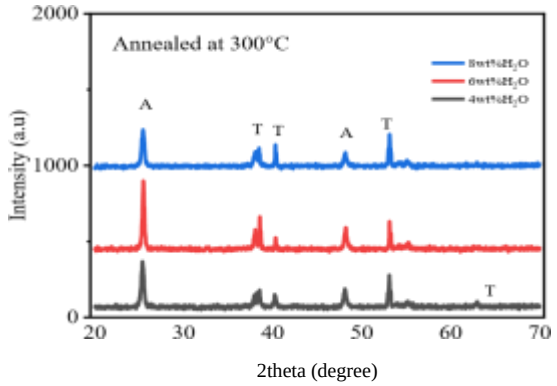

Figure (3) XRD patterns of TiO_2 nanotube samples annealed at 300 ℃ ("A" and "T" stand for- Anatase phase and pure Titanium respectively).

The photocurrent generated from TiO_2 nanotubes in a KOH aqueous solution was measured in the dark. Figure 4 shows a linear sweep voltammogram for TiO_2 nanotubes (4 wt.% H_2O, 6 wt.% H_2O, and 8 wt.% H_2O) annealed at 300 °C in the dark. The peak current densities for electrochemical reduction were obtained from linear sweep voltammograms. The peak current densities are 0.35 mA/cm^2, 0.59 mA/cm^2, and 0.56 mA/cm^2 for TiO_2 nanotubes (4 wt.% H_2O, 6wt.% H_2O, and 8 wt.% H_2O) annealed at 300 ℃ in the dark.

The spectral-dependent current densities of TiO_2 nanotubes (4 wt.% H_2O, 6 wt.% H_2O, and 8 wt.% H_2O) annealed at 300 ℃ were also extracted from linear sweep voltammograms (-1.0 V to 1.0 V) under light illumination with different wavelengths. Figure 4(a-d) shows the linear sweep voltammograms of TiO_2 nanotubes under light with different wavelengths. The current density extracted from linear sweep measurements is tabulated in Table (2).

The higher current for electrochemical reduction under UV light illumination (wavelength 370 nm) is attributed to the larger band gap of TiO_2, which can only be activated under UV. In addition, we found that the photocatalytic activity of TiO_2 nanotubes was significantly influenced by varying the water content in the electrolyte solution. Based on the results (Table 2), under light illumination with a particular wavelength, the TiO_2 nanotubes of the 6 wt.% H_2O sample annealed at 300 °C produced a higher current density, which is attributed to the higher anatase crystalline phase of the TiO_2 nanotubes

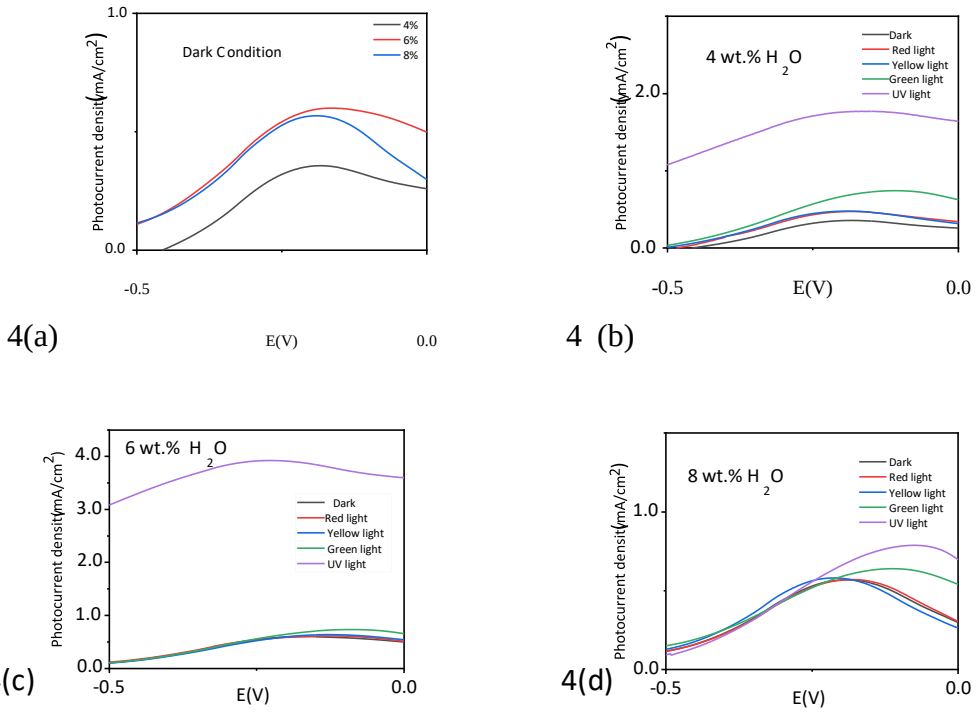

Figure 4(a) Linear sweep voltammograms in dark of TiO_2 (4 wt.% H_2O, 6 wt.% H_2O and 8 wt.% H_2O) nanotubes annealed at 300 ℃. Figure 4(b-d) linear sweet voltammograms of TiO_2 nanotubes (4 wt.% H_2O, 6 wt.% H_2O, and 8 wt.% H_2O) annealed at 300 ℃ under light with different wavelengths (Red, Yellow, Green, UV).

Table 4.2 Spectral dependent photocurrent density of TiO_2 nanotubes

Samples (varying the water content)	**Light sources with wavelength**	**Photocurrent density (mA/cm^2)**	**IPCE%**
Sample(4wt.%H_2O)	Red (665nm)	0.48	0.54
	Yellow (590nm)	0.48	0.61
	Green (515nm)	0.67	0.99
	UV (370nm)	1.76	3.63
Sample(6wt.%H_2O)	Red (665nm)	0.59	0.68
	Yellow (590nm)	0.59	0.77
	Green (515nm)	0.64	0.95
	UV (370nm)	3.92	8.06

Samples (varying the water content)	**Light sources with wavelength**	**Photocurrent density (mA/cm^2)**	**IPCE%**
Sample(8wt.%H_2O)	Red (665nm)	0.57	0.65
	Yellow (590nm)	0.57	0.74
	Green (515nm)	0.59	0.87
	UV (370nm)	0.66	1.36

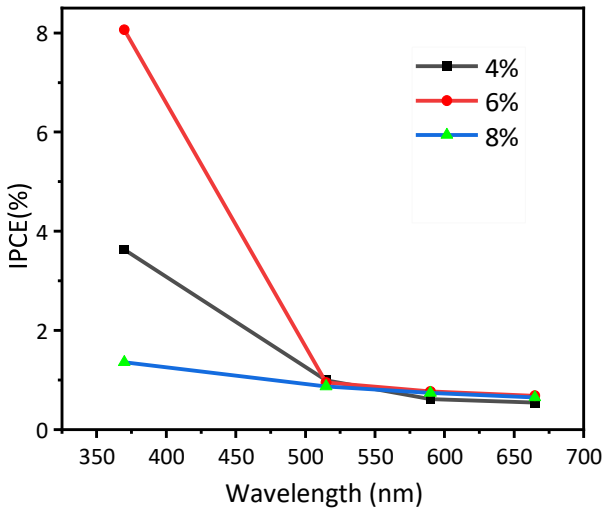

Figure (5) Incident-photon-to-current-efficiency (IPCE %) of TiO_2 nanotubes (4 wt.% H_2O, 6 wt.% H_2O, 8 wt.% H_2O) under light with different wavelengths.

Conclusion

Anodic TiO_2 nanotubes were synthesized by the anodization method by varying the water contents in the electrolyte solution. The influence of the water contents on the TiO_2 nanotubes, physical properties was investigated. Varying the water contents in the electrolyte solution significantly affected the morphology of the nanotubes. One-dimensional TiO_2 nanotubes of diameters 45–50 nm, 55–60 nm, and 50-55 nm has been developed from the respective electrolyte solutions of water content of 4 wt.%, 6 wt.%, and 8 wt.% using the anodization technique. It has been found that the size of nanotubes is not varied according to the water content of the electrolyte solution. Morphology differences could change the value of the band gap energy of the nanotubes. Two processes of oxide layer formation on Ti foil and oxide layer dissolution by fluoride need to be harmonic for the development of well-ordered TiO_2 nanotubes. Among them, well-defined morphologies were achieved in electrolytes with 4 wt.% and 6 wt.% water contents.

The effect of annealing temperature on the formation of crystalline phases of TiO_2 nanotubes was also studied by X-ray diffraction. It was seen that the crystallized sizes of TiO_2 nanotubes decrease as the temperature increases with varying water content in the electrolyte solution. Annealed at 300 ℃ samples, anatase peaks were found. When comparing the anatase peaks annealed at 300 ℃, it was found that the anatase peaks annealed at 300 ℃ have greater

peak intensity. Among the anatase peaks annealed at 300 ℃, the largest peak intensity was found in the 6 wt.% H_2O sample.

The photoelectrochemical response of TiO_2 nanotubes annealed at 300 °C in a KOH aqueous solution was also investigated under illumination with different wavelengths (red, yellow, green, and UV) using linear sweep voltammetry. Under different wavelengths of light, the current densities of the 4 wt.% H_2O and 6 wt.% H_2O samples were the best. But in light with different wavelengths, UV color is better. For all samples, UV light absorption is better because the anatase phase shows better light absorption under UV light.

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