Influence of growth acidic solution and etching time on rutile TiO₂ nanorod arrays synthesized by hydrothermal method in dye-sensitized solar cells

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Titanium butoxide (Ti(OBu)₄) precursor was used to prepare titanium dioxide (TiO₂) nanorods as a photoanode by hydrothermal method directly on FTO glass with different hydrochloric acid (HCl) – water (H₂O) ratio (12.5-7.5, 10-10, 7.5-12.5 and 5-15) ml and etching times (24, 48, and 72)h. The (XRD) results show good crystallinity of TiO₂ with rutile phase and preferred orientations (101) and (002) for all samples. The grain size of the TiO₂ nanorods increases with decrease the HCl concentration. The (FESEM) images show that an increase in HCl concentration leads to an increase in the rod diameter of the TiO₂ NRs and a decrease in their length. The optimum efficiency (η) of DSSC based on TiO₂ NRs was 3.255% at sample ET, where the preparation condition (7.5 ml HCl + 12.5 H₂O) with a 48 h etching time.

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1. Introduction

Dye-sensitive solar cells (DSSC) are still of interest to researchers and companies because the manufacture materials used in there are environment friendly [1-4]. Therefor it can be used in indoor devices that direct contact with humans as system power supply [5–7]. For example, the Internet of Things (IoT) is attracting global scientific and technological attention nowadays since it underlines connections among smart meters, wearable devices, consumer electronic devices, and wireless sensor nodes [8–12]. In addition, the power needed for IoT devices is typically low and can be supplied under room light conditions by running the DSSCs [13–15]. In addition, the DSSC is semitransparent, wherefore it's can be manufactured as large power production panels like sunroofs and house windows [16–20]. Many investigators have made great efforts to enhance the performance of DSSCs by improving the constituents' properties. These efforts can largely be classified into four categories of development: sensitizers, [21-25]anodic materials, [26-29]electrolytes, [30-32] and the modification of anodic materials, especially TiO₂ [33-35]. Apparently, TiO2 has been most frequently used as an anodic material in DSSCs due to its chemical stability and moderate charge transport capability. In addition TiO2 has excellent photoactivity, high-stability, non-toxicity and low cost [36,37]. TiO2 has three different crystalline phases: anatase, rutile, brookite [38-40].

The main objective of this study is to prepare titanium dioxide nanorods on FTO using hydrothermal methods in terms of several conditions. It is found from previous studies that TiO2 nanorod arrays with different dimensions such as rod's length and diameter. So it can be obtained by varying growth conditions, and they are estimated to increase the surface area which is lead to increase the dye adsorption.

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2. Experimental method

2.1. Preparation of /TiO₂ /FTO

The TiO₂ nanorods were prepared with variation of volume of hydrochloric acid and the etching time using hydrothermal methods. The TiO₂ nanorods were prepared on FTO substrate with sheet resistances of ~7 Ω /sq were purchased from Sigma Aldrich using titanium butoxide (Ti(OBu)₄) 97% purchased from Sigma-Aldrich as a precursor (starting material), hydrochloric acid (HCl) as a chelating agent, and deionized water (DI) as a solvent. Chelating agent is ligand that can form bonds (covalent bonding) at more than one point. It is a substance whose molecules can form a several bonds to a single metal ion. Meanwhile, deionized water acts as a function of adding the oxygen (O₂) element into Ti(OBu)₄ for hydrolysis process. First, hydrochloride solvent was prepared by diluting the hydrochloric acid in deionized water to be 20 ml. Then 0.3 ml titanium butoxide (Ti(OBu)₄) was added dropwise into the hydrochloric solvent until the homogeneous mixture was attained. After 20 minutes of stirring the solution will be transparent. The precursor solution was poured into a steel autoclave and followed by placing the FTO substrates vertically into a Teflon-lined stainless steel autoclave. The autoclave was heated in the furnace maintained at 160 °C for 5 h. The experimental details were listed in table (1).

Sample ID	Structure	HCl to distilled water ratio	Etching time	
AT	TiO ₂ / FTO	7.5DW : 12.5 HCL	Overnight	ne .3
BT	TiO ₂ / FTO	10DW : 10 HCL	Overnight	lun le 0
DT	TiO ₂ / FTO	15DW : 5 HCL	Overnight	4 vo In
СТ	TiO ₂ / FTO	12.5DW : 7.5 HCL	Overnight	3u)₄ I Sa m
ET	TiO ₂ / FTO	12.5DW : 7.5 HCL	After 48 H	(O) r al
FT	TiO ₂ / FTO	12.5DW : 7.5 HCL	After 72 H	Ti fo

Table 1. The preparation conditions of TiO_2 nanorods.



Fig. 1. Schematic diagram presents the synthesis of TiO_2 nanorods.

After that, the autoclave was kept into the furnace and cooled down overnight to allow the stainless steel autoclave to cool and touchable. The prepared samples were rinsed with DI water and left to dry at room temperature. Figure (1) summarized the preparation steps of the TiO_2 /FTO nanorods.

2.2. TiCl₄ Treatments

The prepared photo anodes $(TiO_2 \text{ nanostructure})$ were immersed in a 40 mM aqueous TiCl4 solution at ice-cooled conditions for 30 min. Subsequently, the samples were washed with distilled water and rinsed with ethanol to remove any excess of TiCl4 and finally dried. Then, the dried samples were annealed again at 400 °C for 20 min to crystallize attached nanoparticles.

2.3. Counter electrode preparation

Platinum thin films were prepared using Chloroplatinic acid hexahydrate H_2PtCl_6 as reported in the previous paper [41]. 10 mM of H_2PtCl_6 dissolved in absolute ethanol due to its fast evaporation on the FTO substrates using spin coater device maintained at 3600 rpm. Each sample was spin coated for 10 min. The prepared samples were dried at 373 K by a hot plate then they were annealed in the electrical furnace at 723 K for 30 min.

2.4. Cell fabrication

The prepared photo anodes $(TiO_2 \text{ nanostructure})$ were immersed in 0.3mM N-719 $(C_{58}H_{86}N_8O_8RuS_2)$ dye solution for 24 h at room temperature. The working and counter electrode were sealed using a film (Meltonix 45 µm hot melt foil from Solaronix). After the sealing process, a small drop of electrolyte (Iodolyte HI-30) was injected into the fabricated cell.

2.5. Characterization

All of the synthesized samples were analyzed by X-ray diffractometer (Philips PW1730), Cu-K α at λ of 1.54187 Å. The chosen positions of 20 have been chosen within the range of 9.7°-97.9°. (X'Pert HighScore Plus) has been used to obtain the phase and crystallography of the photoanodes. Moreover, the morphological structure and particles distribution of TiO₂ NR have been assessed using scanning electron microscope (FE-SEM) type (TESCAN MIRA₃) and analytic using ImagJ software. The photovoltaic performance of the solar cells can be illustrated by a J-V curve. Current density and voltage (J-V) characteristics of the DSSCs were measured under simulated AM 1.5 sunlight at a light intensity of 100 mW/cm².

3. Results and discussion

3.1. Structural properties of TiO₂

X'Pert High Score Plus software used to match the peaks of synthesized TiO_2/FTO with the stander values JCPDS card. For example, Fig.2. shows the matching of sample BT.



Fig. 2. The matched result of XRD pattern of sample BT using X'Pert High Score Plus software.

The main peaks of the glass slides FTO that attributed to SnO_2 (JCPDS card number 46-1088) are (110), (101), (200), (211), (310), and (301) at $2\theta = 26.65^{\circ}$, 33.7° , 38° , 51.65° , 61.6° , and 65.7° This corresponds to previous researches [42]. Figure (3) shows the crystalline phases of synthesized TiO₂ on FTO substrate with different HCl concentration and etching time. From this figure it was observed that the HCl concentration strongly affects the TiO₂ structure. All TiO₂ samples appear in the rutile phase where the rutile phase is grown in an acidic solvent [43]. The peaks of TiO₂ NRs are attributed to (JCPDS card number 01-076-0649). The rutile phase of TiO₂ was a tetragonal crystalline system with (a,b = 4.593 and c= 2.959) and (α , β , γ = 90°). The peaks of sample BT are (110), (101), (111), (211), (002) and (112) located at $2\theta = 27.55^{\circ}$, 36.29° , 41.46° . 54. 47°, 62.95° and 70.08°; this corresponds to the previous literatures [44]. Sample DT has same peaks of sample BT except (110) and (111) peaks were absent while (210) peak has been appeared at $2\theta = 44.05^{\circ}$ when decrease the acid concentration. At a low acid concentration sample CT (112) vanishes. The TiO₂ nanostructure was grown in the same direction as FTO-film, which means the FTO film plays an important role as a seed layer to grow the TiO_2 . The result can be confirmed because at the synthesis procedure the TiO_2 NRs just adhere on the FTO surface while no film is formed on the other side of the substrate (bare glass) [45–47]. At next the etching time will not change the structure properties [48]. The following peaks intensity (101) and (002) decrease with increased of etching time. These peaks may determine the length of TiO_2 NRs because the height of TiO₂ NRs is directly proportional to the intensity of the previous peaks that proposed a TiO_2 NRs grown in (101) and (001) direction within the vertical axis of growth to the FTO substrate [47]. This result can be confirmed by FESEM images. The grain size of TiO₂ nanostructures are listed in Table (2). TiO_2 grain size of main peaks (101) and (003) are reduced with decrees the HCl concentration whereas has same behavior with increasing the etching time. These behaviors will be explained in FESEM section.



Fig. 3. XRD pattern of all synthesized sample of TiO₂ NRs.

Sample	20	d-spacing (A)	FWHM	hkl	Crystalline
BT	27.540	3.415	0.295	110	27.708
	36.298	2.608	0.197	101	42.481
	41.470	2.293	0.590	111	14.388
	54.469	1.771	0.394	211	22.700
	62.910	1.551	0.246	002	37.857
	70.082	1.408	0.344	112	28.174
СТ	36.097	2.622	0.316	101	26.441
	44.199	2.157	0.256	210	33.493
	54.483	1.771	0.600	211	14.882
	62.795	1.554	0.336	002	27.700
	64.613	0.295	0.543	301	17.310
DT	36.073	2.624	0.226	101	36.919
	44.199	2.157	0.232	210	36.958
	54.429	1.772	0.600	211	14.879
	62.839	1.553	0.274	002	34.025
	64.462	1.517	0.492	301	19.077
	69.823	1.413	0.447	112	21.653
ET	36.103	2.622	0.296	101	28.228
	44.199	2.157	0.239	210	35.875
	62.811	1.554	0.279	002	33.326
	64.096	1.525	0.504	301	18.585
	69.875	1.412	0.477	112	20.299
FT	36.101	2.622	0.256	101	32.639
	44.199	2.157	0.250	210	34.283
	62.747	1.555	0.327	002	28.420
	64.156	1.524	0.551	301	17.007
	69.913	1.411	0.509	112	19.036

Table 2. The structural analysis of TiO_2 NRs.

3.2. Morphological properties of TiO₂ NRs

The morphological structure and particles distribution of TiO_2 NR have been assessed using SEM analysis. Figure (4) shows the SEM Images of the TiO_2 samples synthesized using hydrothermal methods on FTO substrate with different HCl concentration and etching time. The magnification of the previous figure is 5Kx. These images are shown the TiO_2 NR surface grown on the FTO surface. The TiO_2 NRs were evenly distributed over FTO substrate. On the other hand, EDX results shows the contents of the optical electrode of all synthesized samples are clear from the impurities as shown in Fig. 5.



Fig. 4. SEM Images of the TiO₂ samples with 5Kx magnification: a. BT, b. CT, c. DT, d. ET, and e. FT.



Fig. 5. EDX results of TiO₂/FTO.

Figure (6) shows SEM cross-section images for BT sample. The diameter of TiO_2 is very low and close together. Consequently, large clumps were formed of the TiO_2 NR. The TiO_2 NRs are tetragonal in shape with square top facets, the expected growth habit for the tetragonal crystal structure. The average diameter and length are 170 nm and 4.0 μ m, respectively where exhibited in last figure and listed in Table 3.



Fig. 6. SEM cross-section images for BT sample.

SEM cross-section images for CT and DT samples are shown in Figures (7 and 8) consecutively. From these figures, it was obtained that the distance between TiO_2 NR increased with decreased HCl concentration. Furthermore, the lengths of TiO_2 NR decreased and the average diameter are increased as shown in Figure (11) and listed in Table 3.



Fig. 7. SEM cross-section images for CT sample.



Fig. 8. SEM cross-section images for DT sample.

The lengths and the average diameter of TiO_2 NRs are changed with different HCl volume. So, to discuss the effective of HCl concentration on the structure and morphological

properties of TiO_2 NRs, it was must be study the chemical reaction between HCl, H_2O and Ti(OBu).

The following procedure is used to describe the creation of rutile crystal nuclei in $Ti(OCH_2CH_2CH_2CH_3)_4$ highly acidic precursor solution. The hydrolysis of $Ti(OCH_2CH_2CH_2CH_3)_4$ produces a single polymer $[TiO(OH_2)_5]_{2+}$. This in turn joins together by dehydrating each other to create a straight chain polymer. Finally, several points connect the straight chain polymers to form the rutile crystal nucleus. In the other side, titanium (IV) butoxide react with water as a fallowing equation [49]:

$$Ti(OBu)_4 + 2H_2O \rightarrow TiO_2 + 4 HOBu$$
(1)

Heat treated TiO₂ NPs coated onto FTO can be used as seeds of heterogeneous nucleation based on heterogeneous nucleation of crystalline phase in solution. The formation of NRs can be accomplished through the deposition and rearrangement of TiO_2 seeds during dynamic chemical dissolution and deposition procedure. Furthermore, when TiO_2 growth units deposit on TiO_2 crystal seeds, a strong HCl acid plays an important function, and it can encourage TiO₂ crystals to grow into rods rather than particles [47]. It can be concluded that the high HCl concentration, water content is too low, not enough to form TiO₂ to produce seed layer and coated onto FTO. Therefore, it can be explained the Non-adhesion of TiO_2 NRs on FTO in sample (AT) because the seed layers were not formed. In contrast, when HCl decrease the H₂O volume is increased therefore TiO₂ seed layers are formed onto the FTO substrate. This leads to grow of TiO₂ NRs onto the FTO surface as in sample BT. Finally, when the water concentration increase it may lead to increase the seed layer diameter. This fact may explain the inverse proportion between HCl concentration and TiO₂ NRs diameter [50]. Although good TiO₂ NRs are gotten, but the FESEM images show the presence of lumps and agglomerate between the TiO₂ NRs. These conglomerates may lead to reduce the surface area of the photo-electrode. The etching strategies are expected to improve the photo-electrode performance [51]. Figures (9 and 10) present the TiO₂ NRs after etching time (48 and 72 h) at room temperature. The etching time leads to a decrease in the TiO_2 diameter and length. The etching process removes the agglomerate particle on the top of the sample DT. Where the top of the etched sample ET appears as a brush compared with the untreated surface sample DT.



Fig. 9. The cross-section and SEM Images of sample ET.



Fig. 10. The cross-section and SEM Images of sample FT.





Fig. 11. Histogram chart of the diameter distribution of TiO₂ NRs.

Figure (11) display the histogram chart of TiO_2 NRs diameter distribution. TiO_2 NRs diameter distribution is strongly affected by HCl concentration obtained from the FESEM result using ImagJ software of TiO_2 NRs diameter distribution was discussed in previous.

Sample	high (µm)	Average diameter (nm)
BT	4	170
СТ	1.68	27.3
DT	3.85	22
ET	3.8	19.2
FT	1.43	18.9

Table 3. Lengths of TiO_2 NRs and the average diameter.

3.3. J-V characterization of TiO₂

The J-V results of TiO_2 films prepared on FTO substrates using a hydrothermal method with different HCl concentration and the etching time was shown in Fig. 12). These results reported that the conversion efficiency of the highly effected by the preparation condition parameter where the solar cell efficiency of the fabricated cell are (2.067, 0.889, 2.959, 3.255 and 1.389) for (BT, CT, DT, ET and FT) respectively. While the open-circuit voltage (V_{oc}) of all samples remained constant at (0.7 V) except sample (CT) recorded at (0.68 V) due to the fact that the sample (CT) which has a low thickness and high grain size which lead to increase the recombination process of the electron in the conduction band of the TiO₂ with electrolyte energy level [52].

The short circuit current density (Jsc) is directly proportional to the solar cell efficiency of the fabricated cell. JSC is affected by several factors as dye molecular structure, amount of dye adsorbed on photoanode, and electrochemical properties of photoanode in the presence of electrolyte [53,54]. Therefore the variation of the Jsc was observed from the modification of TiO_2 structure where the modification of TiO_2 electrode structure increased the internal surface area of the electrode to allow a large enough amount of dye to be contacted simultaneously by the TiO_2 electrode and the electrolyte. As a result, Photo-electron excitation was increased which led to increasing the short circuit current density. Therefore large surface area for dye absorption is the basic requirement for photoanode material [55]. These results are strengthening the SEM results of TiO_2 nanorods where the HCl concentration was used to control the number of TiO_2 rods per unit area whereas the etching time led to increase the porosity of the TiO_2 nanorods.

The photocurrent-voltage parameters such as open circuit voltage (Voc), short circuit current density (Jsc), fill factor (FF) and cell conversion efficiency (η) as well series resistance (Rs) and shunt resistance (Rsh) are estimated from the J-V curves a tabulated in Table 4.



Fig. 12. J-V curves of the DSSCs based on TiO₂ NR PEs.

Sample ID	J sc	Voc	Jm	Vm	η	F.F.	$R_{s}(\Omega)$	R_{sh} (Ω)
BT	4.413	0.700	3.690	0.560	2.068	0.669	251.6	9663.8
СТ	1.952	0.680	1.646	0.540	0.889	0.670	552.2	20660.7
DT	6.011	0.700	5.285	0.560	2.960	0.703	152.1	12411.9
ET	6.381	0.700	5.906	0.551	3.255	0.729	163.2	13526.9
FT	2.942	0.700	2.481	0.560	1.390	0.675	317.2	13885.7

Table 4. the DSSCs parameters of the TiO_2 NR PEs.

Additionally, the fill factor (F.F) is yet another important parameter that reflects the quality of solar cells. The fill factor (F.F) is a measure of the squareness of the curve, which are used to determine efficiency (η). The fill factor (FF) was improved from 0.669 to 0.729 Therefore; the length of TiO₂ nanorods significantly improved the performance of DSSC including Jsc, Voc, and fill factor [56,57]. For DSSC, large surface area meant more dye molecules could be attached on TiO₂ nanorods, which would be tremendously increased the current density. The improvement of F.F indicated that the recombination between electron and holes, and scattering during electron transportation were less [58–60].

Finally, increasing the shunt resistance and decreasing the series resistance as well as reducing the overvoltage for diffusion and electron transfer will lead to a higher FF value, thus resulting in greater efficiency and pushing the output power of the solar cell [61–63].

4. Conclusion

Titanium butoxide (Ti(OBu)4) precursor used to prepare titanium dioxide (TiO₂) nanorods as a photoanode using hydrothermal method directly on the FTO glass with different hydrochloric acid (HCl) – water (H₂O) ratio and etching time. The acidic medium provided rutile phase structures with preferred orientations (101) and (002) of the TiO₂ samples. Moreover, the increase of HCl concentration leads to an increase in the rod diameter of the TiO₂ NRs and a decrease in the length as exhibited in SEM Image. While the etching time leads to a decrease in the diameter and length of the TiO_2 nanorods. Finally, the dye adsorption is highly depending on the TiO_2 surface area which leads to improve the DSSC performance.

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