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Effect of Electrolyte Composition on Structural and Photoelectrochemical Properties of Titanium Dioxide Nanotube Arrays Synthesized by Anodization Technique

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Abstract:

The present work involves studying the effect of electrolyte composition [$@1= 0.5 \text{ wt.} \% \text{ NH}_4\text{F} / 5\% \text{ H}_2\text{O} / 5\% \text{ Glycerol (GLY)} / 90\% \text{ Ethylene Glycol (EG)}$] and [$@2= 0.5 \text{ wt.} \% \text{ NH}_4\text{F} / 5\% \text{ H}_2\text{O} / 95\% \text{ Ethylene Glycol (EG)}$] on the structural and photoelectrochemical properties of titania nanotubes arrays (TNTAs). TNTAs substrates were successfully carried out via anodization technique and were carried out in 40 V for one hour in different electrolytes ($@1$, and $@2$). The properties of physicochemical of TNTAs were distinguished via an X-ray Diffractometer (XRD), Field Emission Scanning Electron Microscope (FESEM), an Energy Dispersive X-ray (EDX), and UV-visible diffuse reflectance. The photoelectrochemical response of TNTAs was evaluated in 0.01M Na₂S under the choppy light of a halogen lamp. TNTAs photoelectrode prepared at $@1$ electrolyte was not sufficient to increase the photocurrent response compared to TNTAs prepared at $@2$. The TNTAs photoelectrode prepared in the $@2$ electrolyte confirmed the highest photoconversion efficiency compared to the TNTAs photoelectrode prepared in the $@1$ electrolyte.

Key words: Electrolyte composition, Glycerol, Photoconversion efficiency, Photoelectrochemical cell, Titania nanotubes.

Introduction:

Over the previous decades, the preparation and characterization of nanostructure as one dimensional (1-7), in particular, nanotubes form attracted intensive technological and scientific attention due to the series of rousing features (like non-bulk properties, directionality, and high surface area,) in addition to their applications in sensors, fuel cells, capacitors, solar cells, photoelectrochemical cells, etc. Generally, efforts concentrate on the use and the production of carbon-based nanotubes, in the past 10 years also nanostructured of metal-oxide. For example, titanium dioxide nanotubes arrays (TNTAs) have attracted growing attention because TNTAs is of large scientific benefit as it displays adorable properties that can be used in many applications. Thus, large studies have concentrated to prepare TNTAs via different techniques like a synthesis of

template, sol gel, hydrothermal process, and anodization technique. Among the several paths to produce TNTAs nanostructures, a generally simple way is the anodization of titanium foil in fluoride electrolyte (8-12). The anodization technique is deemed to be highly advantageous, productive, and favorable due to the production of well-aligned, steady, and so ordered TNTAs. TNTAs can be synthesized simply from the substrate of Ti foil. Additionally, this technique is a cost-effective, simple procedure as temperature and elevated vacuum existence is needless. Anodization method in fluoride electrolyte can be executed under the self-organizing case and can be modified to lead to quite ordered arrays of pores or closely vertically tubes. Over the last few years, great progress has been done, in particular, to optimize morphology of TiO₂ nanotubular (13-15). The suitable heat

treatment can convert the amorphous tubes formed by an electrochemical method to rutile or an anatase crystalline form in order to use the crystalline form (anatase) for many applications (16,17). The chemical and physical features of the TNTAs are reliant on conditions of growth (18), so by changing the growth parameters as a time of anodization, electrolyte composition, and applied potential to form TNTAs. The morphology of the TNTAs can be improved and the best TNTAs can be attained (19). For instance, amongst the parameters of growth, the voltage of anodization is the main factor that effects on the diameters of nanotube (20). The goal of this work is to examine the influence of the electrolyte composition on the physical, morphological, and photoelectrochemical response features of TNTAs via UV-visible diffuse reflectance spectroscopy, FESEM, EDX, XRD, and a linear sweep photovoltammetry (LSPV) analyses and find the optimum electrolyte composition.

Materials and Methods

Preparation of TNTAs

The first step, Ti foil (99.9 %, 0.1 mm thickness) (Wuhan Kemi-Works, Chemical Co. Ltd/ China) was cut into a rectangular size of (2 x 1) cm with an extra 0.5 cm acting as a holder of the TNTAs electrode (Fig.1). The Ti foil was degreased by sonication in acetone, isopropanol, and deionized water (DI) for fifteen minutes (21). Then, 6 M HNO₃ was used for being chemically etched for 10 min in order to form a smooth surface (21). After that, the Ti foil was rinsed with DI water and left to dry in air.

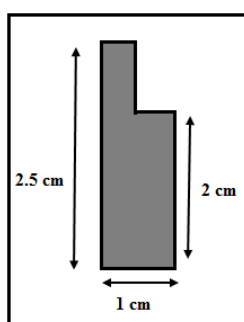


Figure 1. Schematic outline of Ti foil

Anodization method was executed at constant voltage (40 V) for one hour utilizing a DC power supply (MCH-5010D)(Fig.2). The different electrolytic composition was used to prepare TNTAs as mentioned below:

(@1) 0.5 wt.% NH₄F / 5% H₂O / 5% Glycerol (GLY)/ 90% Ethylene Glycol (EG).

(@2) 0.5 wt. % NH₄F / 5% H₂O / 95% Ethylene Glycol (EG). Then, the resulting films were washed

with DI water. Finally, the products were annealed at 500 °C for two hours.

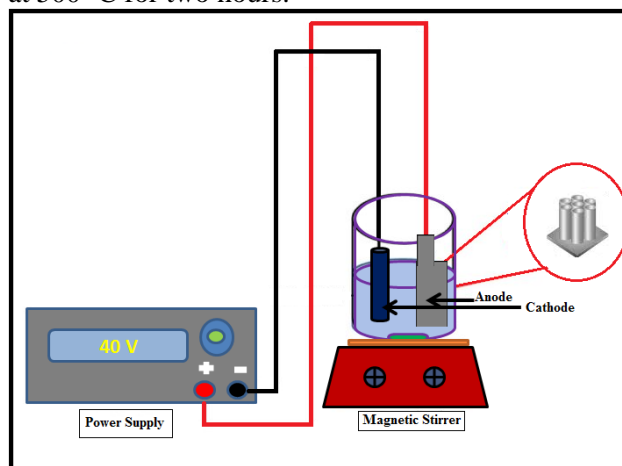


Figure 2. Set up for anodization method

Characterization of TNTAs

The absorption spectra of TNTAs electrodes were determined by UV-visible diffuse reflectance spectrophotometer (Cary 500 UV-DRS, USA Varian Company). On the other hand, the field emission scanning electron microscopy (FESEM, Carl Zeiss SUPRA 40VP) was applied to recognize the morphologies of the TNTAs electrodes and the energy dispersive x-ray (EDX) spectrometer was done to analyse elementals. The X-ray diffractometry (XRD) (X' Pert Pro-MPD, PANalytical with CuK α radiation, $\lambda = 1.504 \text{ \AA}$) was executed in order to determine the structures of TNTAs.

Photocurrent response of TNTAs

The photocurrent response of TNTAs prepared at different electrolyte (@1 and @2) was measured by intermittent irradiating the TNTAs electrodes from halogen lamp using linear sweep photovoltammetry by using (AUTOLAB) with scanning a potential sweep from (+1 to -1) V. The experiment was carried out using a three-electrode photoelectrochemical cell with TNTAs as the working electrode, Ag/AgCl as the reference electrode, and Pt wire as the counter electrode in 0.01M Na₂S.

Result and Discussion:

Figure 3A and B displays FESEM images of sample anodized in different electrolytes @1 and @2 respectively. Clearly, the TNTAs are attached to each other and the external walls demonstrate several undulations that will raise the roughness of the surface (Fig. 3A). As a proposition by means of Macak et al. (15), these undulations may be created because the fluctuations of current happen through the anodization procedure or, oppositely, the variation of current may occur by the created

undulations (22-23). The TNTAs obtained in @1 have a tube length of 2.2 μm as shown in Fig. 3C. Moreover, TNTAs obtained in @2 electrolyte was a clean and smooth wall, while the length of the tube

is 2.7 μm (Fig. 3D). Furthermore, the diameter and wall thickness of TNTAs in @1 and @2 electrolytes are displayed in Table 1.

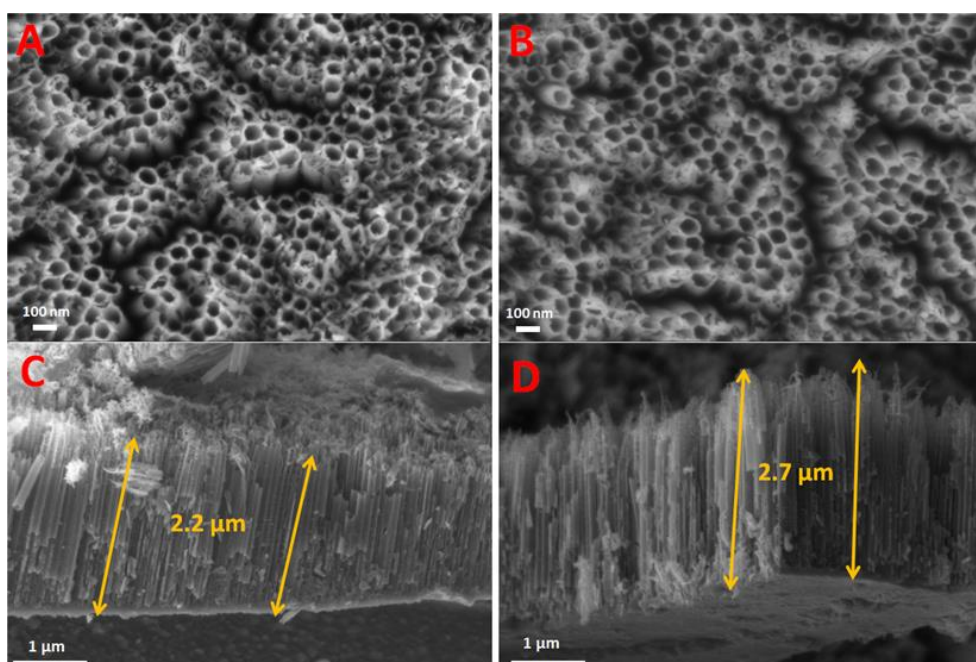


Figure 3. FESEM images of TNTAs prepared in (A)= @1, (B)= @2, (C) cross-sectional FESEM image of TNTAs in @1, and (D) cross-sectional FESEM image of TNTAs in @2

Table 1. the diameter and wall thickness of TNTAs prepared in electrolytes (@1 and @2)

Sample	Diameter (nm)	wall thickness (nm)
TNTAs in @1	44-68	17±4
TNTAs in @2	47-71	14±2

The decrease of the length and diameter of TNTAs formed in the electrolyte containing glycerol can be explained due to increasing the viscosity of the electrolyte. There are two processes affected via the electrolyte viscosity:

- a- The chemical dissolution rate of the tubes at the top of the nanotubes
- b- The rate of growth at the nanotube bottom.

As mentioned by Ahmed El Ruby et al. (24), the electrolyte viscosity has a direct effect on the

spread of reactants and products from and to the surface of titania nanotubes. Furthermore, the viscosity has a negative effect on the growth rate and the synthesis of titania nanotubes. The rate of growth was low in glycerol electrolytes and the addition of water enhanced the rate of growth due to the reduction in the viscosity of electrolyte. Ethylene glycol is a lower viscous compared to glycerol and results in lower resistance of diffusion. Therefore, the rate of growth would be higher in ethylene glycol electrolytes.

The presence of TiO_2 has been proven by the presence of Ti and O species that have been detected in EDX analysis as shown in Fig. 4 A and B.

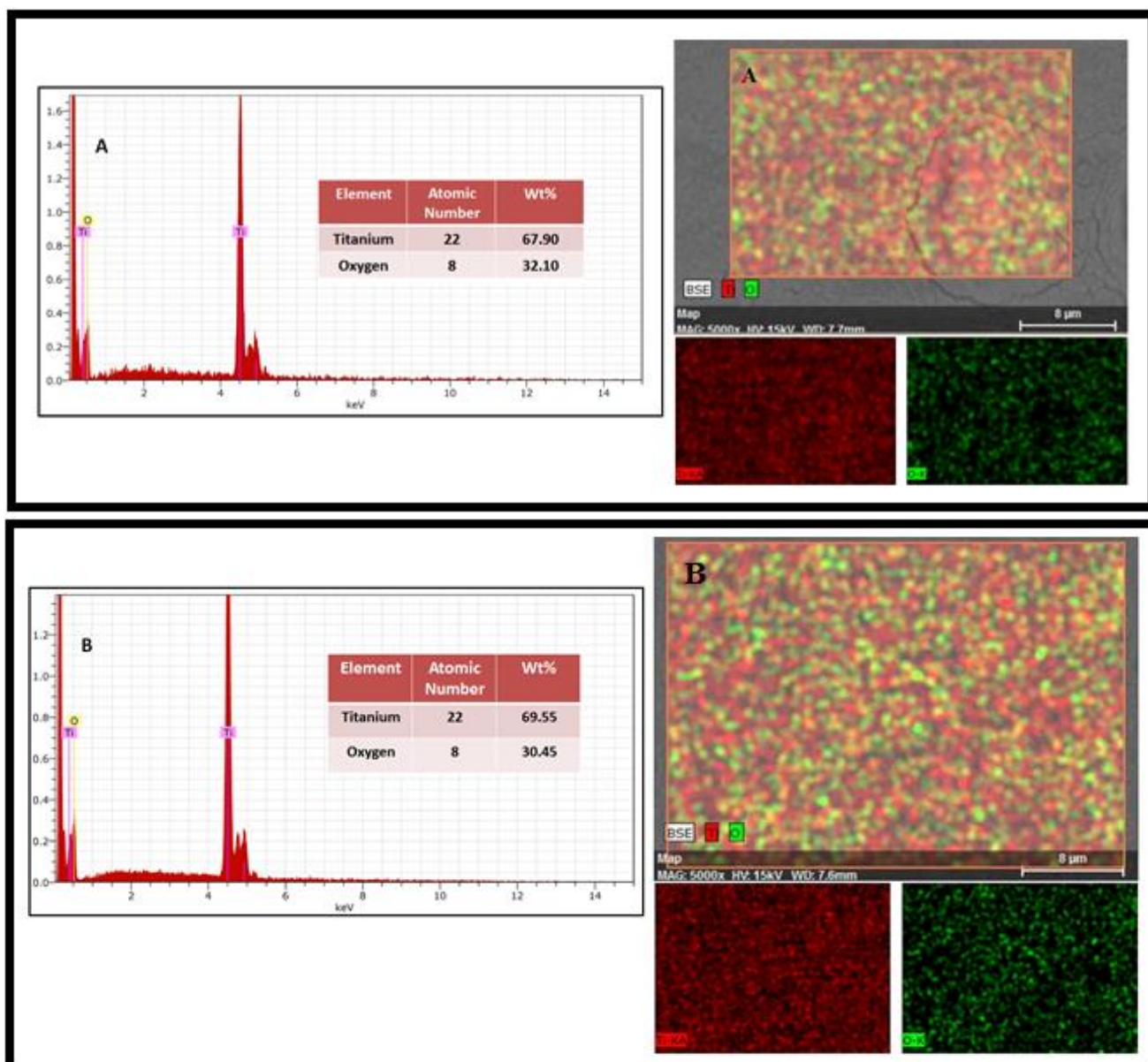


Figure 4. EDX elemental composition data and MAP of TNTAs prepared in (A) = @1 and (B)= @2

From the diffractograms in Fig.5, TNTAs display diffraction peaks of Titanium (JCPDS 00-044-1294) at $2\theta=35.8^\circ$, 38.04° , 39.9° , 52.8° , and 77.8° corresponding to [100], [002], [101], [102], and [201] respectively. In both of the samples, it was observed that the notable distinctive peak of anatase (JCPDS 00-021-1272) was at $2\theta=25.1^\circ$ corresponding to [101], followed by other peaks of anatase at $2\theta=36.7^\circ$, 54.9° , 62.6° , 68.7° , 70.4° , 74.9° , 76.02° , and 82.1° that correspond to [103], [211], [204], [116], [220], [215], [301], and [303] respectively. Furthermore, small peaks of rutile at $2\theta=27.27^\circ$, 44.30° , and 64.69° were also displayed that corresponds to [110], [210], and [310] respectively (JCPDS 00-021-1276). These results prove that the TNTAs obtained minor consist of rutile and a major anatase structure.

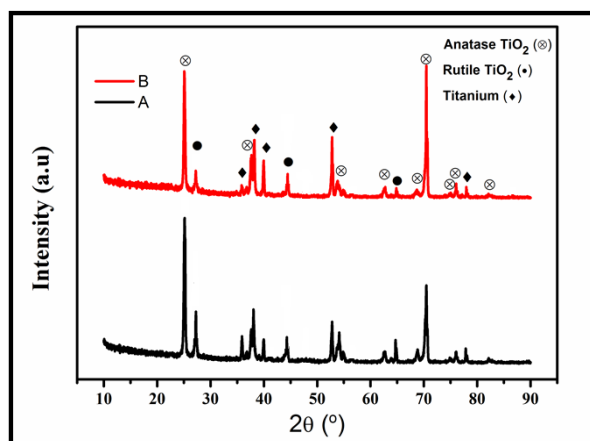


Figure 5. XRD diffractograms of TNTAs prepared in (A) = @1 and (B)= @2

Figure 6 demonstrates the UV-DRS curves of TNTAs fabricated at different electrolytes @1 and @2, it is shown that both TNTAs exhibited strong

UV light absorption at $\lambda < 400$ nm that was due to real band gap of TiO_2 (25).

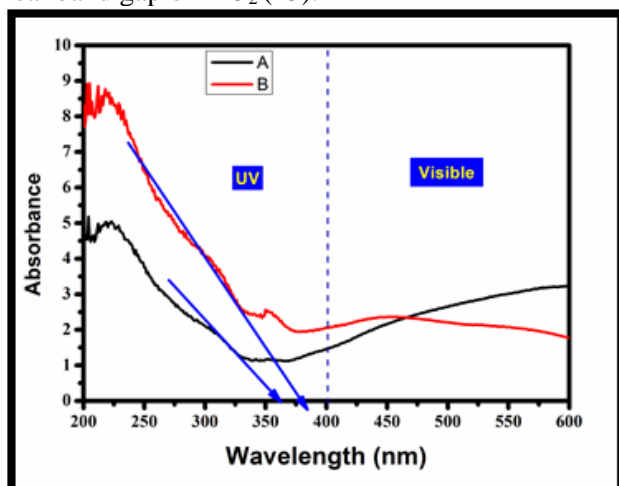


Figure 6. UVDRS spectra of TNTAs prepared in (A) = @1 and (B) = @2

The photoelectrochemical cell (PEC) performance of TNTAs was assessed by the performance of photoconversion efficiency (η) calculated using Equation 1 where I_0 (mA/cm^2) refers to the photocurrent density gained by deducting the dark current from photocurrent as displayed in Fig. 7. Furthermore, V bias points to the chosen potential bias to calculate I_0 as illustrated in Fig. 7. While J light (mW/cm^2) point to the power of light irradiance.

$$\eta = \frac{I_0 (1.23 - V_{\text{bias}})}{J_{\text{light}}} \times 100 \quad (\text{Eq. 1})$$

Figure 7 shows the photocurrent response of TNTAs fabricated in @1 and @2 electrolytes under choppy irradiation, which was estimated at 0.01 M Na_2S . From the graph of I-V, it is observed that TNTAs fabricated in @2 electrolyte exhibited a higher photoresponse compared to TNTAs fabricated at @1 electrolyte. This displays that the photoresponse of TNTAs could not be modified when the electrolyte consisting of glycerol. This could be confirmed by the dropped of photoconversion efficiency ($\eta = 0.006\%$) as shown in Fig. 8.

Moreover, the highest photocurrent response obtained for TNTAs in @2 is due to the longest tube length gained (2.7 μm), compared to TNTAs obtained in @1 (2.2 μm). According to Lim et al. (26) the large surface area raises linearly with the increasing length of the tube. So, the higher photocurrent density for TNTAs prepared at @2 electrolyte was ascribed to the higher active surface area that enhances the light-gathering capability and better absorption of a photon of this photoanode.

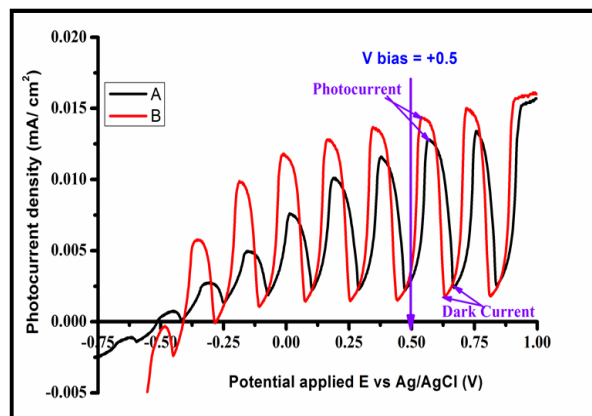


Figure 7. I-V graph of TNTAs prepared in (A) = @1 and (B) = @2

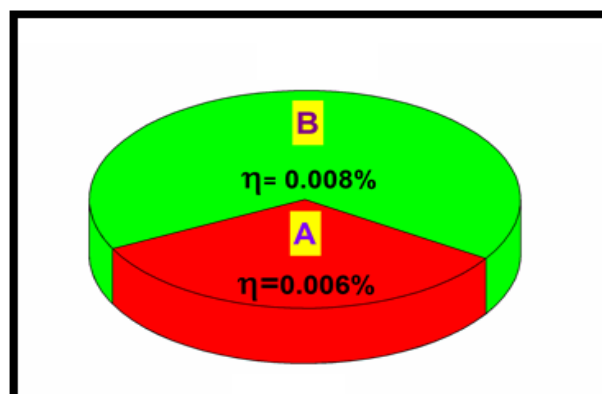


Figure 8. Photoconversion efficiency ($\eta\%$) of TNTAs prepared in (A) = @1 and (B) = @2

Conclusion:

Electrolyte Composition plays an important factor in influencing the crystalline structure, morphology, geometry, photocurrent response, and photoconversion efficiency of in electrochemical fabricated of titania nanotube Arrays (TNTAs). In this study, 2.7 μm of TNTAs fabricated in @2 produces the higher photoconversion efficiency ($\eta = 0.008\%$), that is upper than the efficiency for TNTAs fabricated in @1 ($\eta = 0.006\%$). This research has confirmed if a little content of water in the electrolyte used to prepare TNTAs could fit to enhance and increase its photocurrent response. Furthermore, when the viscosity of the electrolyte increases by using glycerol and ethylene glycol to prepare TNTAs, the photocurrent response of the TNTAs electrode decreases and produces lower photoconversion efficiency.

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Authors' declaration:

- Conflicts of Interest: None.

- We hereby confirm that all the Figures and Tables in the manuscript are mine ours. Besides, the Figures and images, which are not mine ours, have been given the permission for re-publication attached with the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee in University of Baghdad.

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تأثير مكونات المحلول الالكتروليتي على الخواص التركيبية والخواص الكهروكيميائية الضوئية لمصفوفات الانابيب النانوية للتيتانيا المحضرة بواسطة تقنية الأنودة

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الخلاصة:

العمل الحالي يتضمن تأثير مكونات المحلول الالكتروليتي

[@1= 0.5 wt.% NH₄F / 5% H₂O / 5% Glycerol (GLY)/ 90% Ethylene Glycol (EG)] and [@2= 0.5 wt. %
NH₄F / 5% H₂O / 95% Ethylene Glycol (EG)].

على التركيب والخصائص الكهروكيميائية الضوئية للانابيب النانوية تيتانيا. تم تحضير ركائز التيتانيا بنجاح بواسطة تقنية الأنودة والتي
اجريت عند 40 فولت ولمدة ساعة وفي محاليل الكتروليتية مختلفة. شخّصت الخواص الكيميائية الفيزيائية لـ TNTAs باستخدام مقياس حيود
الأشعة السينية (XRD)، المجهر الإلكتروني (FESEM)، والأشعة السينية المشتتة للطاقة (EDX)، والانعكاس الطيفي للأشعة فوق
البنفسجية. تم تقييم الاستجابة الكهروضوئية لـ TNTAs في (0.01 M Na₂S) تحت ضوء متقطع من مصباح الهالوجين. لم يكن قطب
TNTAs المعد في المحلول الالكتروليتي @1 كافيًا لزيادة استجابة التيار الكهروضوئي مقارنة بـ TNTAs المعد في @2. أظهر القطب
TNTAs المعد في حل @2 أعلى كفاءة للتحويل الضوئي بالمقارنة مع TNTAs الأخر.

الكلمات المفتاحية: مكونات الالكتروليت، الجليسيرول، كفاءة التحويل الضوئي، الخلية الكهروكيميائية الضوئية، تيتانيا نانوتيوب.