Production of titanium oxide nano wires with bundle structure using single anodic process

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Abstract

In a single process, the surface of Ti was transformed into titanium oxide nanowires (TNWs) at room temperature. The rapid breakdown anodizing method (RBA) of producing deposited spherical nanoparticles was modified. Instead, TNWs attached to the Ti metal base were formed. To slow down the reactions of these processes, 25,50, and 75wt % glycerol were added separately to the anodizing solution of RBA. The results of the X-ray diffraction (XRD) tests revealed the amorphous structure of the formed TNWs for all samples. The produced TNWs had the shape of micro bundles with nanowires. Their diameters were less than 50 nm, as shown by scanning electron microscope (SEM) images. The prevalence of titania bundles was more intense when a lower amount of glycerol was used. The tallest length of the nanowires decreased from 32μm to 8μm with the increase of glycerol; so by using a suitable electrolyte solution, the anodizing process can be effective for controlling the size of TNWs. The decrease in atomic percent oxygen with increasing glycerol was confirmed by energy dispersion X-ray (EDX) spectra.

Keywords: Anodic process; bundle structure; glycerol; nanowires; titania.

1. Introduction

RBA technique was used to produce nano-oxides for different purposes, such as bioactive materials, sensors, and photocatalytic decolorization (Saima *et al*., 2018; Mustafa & Reem, 2020; Reem & Mustafa, 2020). This method provides a cheap and simple way to produce different nano oxides deposited on different bases with dissimilar shapes and compositions. Utilizing this technique; Mustafa *et al*. produced nanoparticles as precipitated powders of different materials such as ZnO, Cu_2O, MgO, and TiO_2 (Mustafa *et a*l., 2021). In order to use these powders in some applications, like, for example, sensors; a deposition technique must be used to deposit them on appropriate bases. An electrophoretic deposition technique was used to deposit TiO_2 that was produced by RBA on a Ti base to use it as a gas sensor (Reem & Mustafa,2019). The process of forming precipitated nanopowders and using another technique to deposit them on suitable bases can be shortened by one process, as in the present work.

In general, the methods for producing TNWs can be divided into two categories: hydrothermal and anodizing techniques; but the production of these nano products by the anodizing method is not a one-step process. Usually, TiO_2 nanotubes (TNTs) are converted into TNWs in different ways, Ming *et al*., fabricated TNWs connected directly with TNTs arrays

following four stages and using two successive anodic processes with different conditions (Ming *et al*., 2012). Even nanowires made of materials other than titanium oxide often require more than one step; Xiangming *et al*. prepared Cu nanowires using a two-step approach and further studied the thermal oxidation behavior of Cu nanowires in dry oxygen (Xiangming *et al*., 2021).

Most of the processes that produce nanowires need temperatures greater than room temperature. The hydrothermal process involves relatively high temperatures and pressures (Wenxian *et al*., 2018). Endre *et al*.,2007 used the hydrothermal conversion of self-assembled TNTs into nanowires in a revolving autoclave (Endre *et al*., 2007). When TNTs are manufactured at temperatures exceeding 400°C, nanowires are commonly detected (Shalini *et al*. 2021). Poudel *et al*. transformed TNTs to TNWs by annealing at 650^0C (Poudel *et al*., 2005). The electro spinning technique followed by annealing was also utilized to fabricate well-aligned TNWs with different crystal phases (Zhou *et al*., 2019).

With this participation, an attempt was made to convert Ti to TNWs at room temperature by using a simple, cheap, and one -step process.

2.Experimental details

After cleaning with absolute alcohol (from Sigma-Aldrich, USA), 0.1 mm thick Ti foils (from Ti foil manufacturer - Baoji Energy Titanium Co, China) with a rectangular shape (1x2 cm^2) were immersed in an electrolyte. This electrolyte was made up of 0.1 M $HClO_4$ (from Sigma-Aldrich, USA) and glycerol (from Phywe, Germany). Three volume percent of 25, 50, and 75% glycerol were added separately to slow down the reactions. The viscosity was measured by hand viscosity meter (Viscolite), PCE Instruments UK Ltd. Table 1 displays some properties of the solutions used in this work. During each electrochemical process, two Ti pieces were used, one as a working electrode (anode) and the other as a control (cathode). The applied voltage was 20 volts, and the distance between the two electrodes was 0.5 cm. The time of the process was 30 minutes at room temperature. The produced surfaces were tested using XRD techniques (Shimadzu X-ray diffractometer-6000)-Japan. The particle sizes and appearances were evaluated using (SEM+EDX), from (ZEISS EVO LS10- Germany. The prepared samples were optically micrographed using an optical microscope (KERN Transmitted light microscope OBL-1)-Germany.

Table1. Density and viscosity of glycerol/water mixtures.

	Glycerol 25%	Glycerol 50%	Glycerol 75%
Density of mixture [kg/m^3]	1053.1	1136.5	1211.1
Dynamic viscosity of mixture [$N\ s/m^2$]	$1.52*10^{-3}$	$5.69*10^{-3}$	$4.96*10^{-2}$
Kinematic viscosity of mixture [m^2/s]	$1.44*10^{-6}$	$5*10^{-6}$	$4.1*10^{-5}$

3.Results and discussion

The microbundles with nanowires resulting from the modified RBA process are shown in Figure 1.

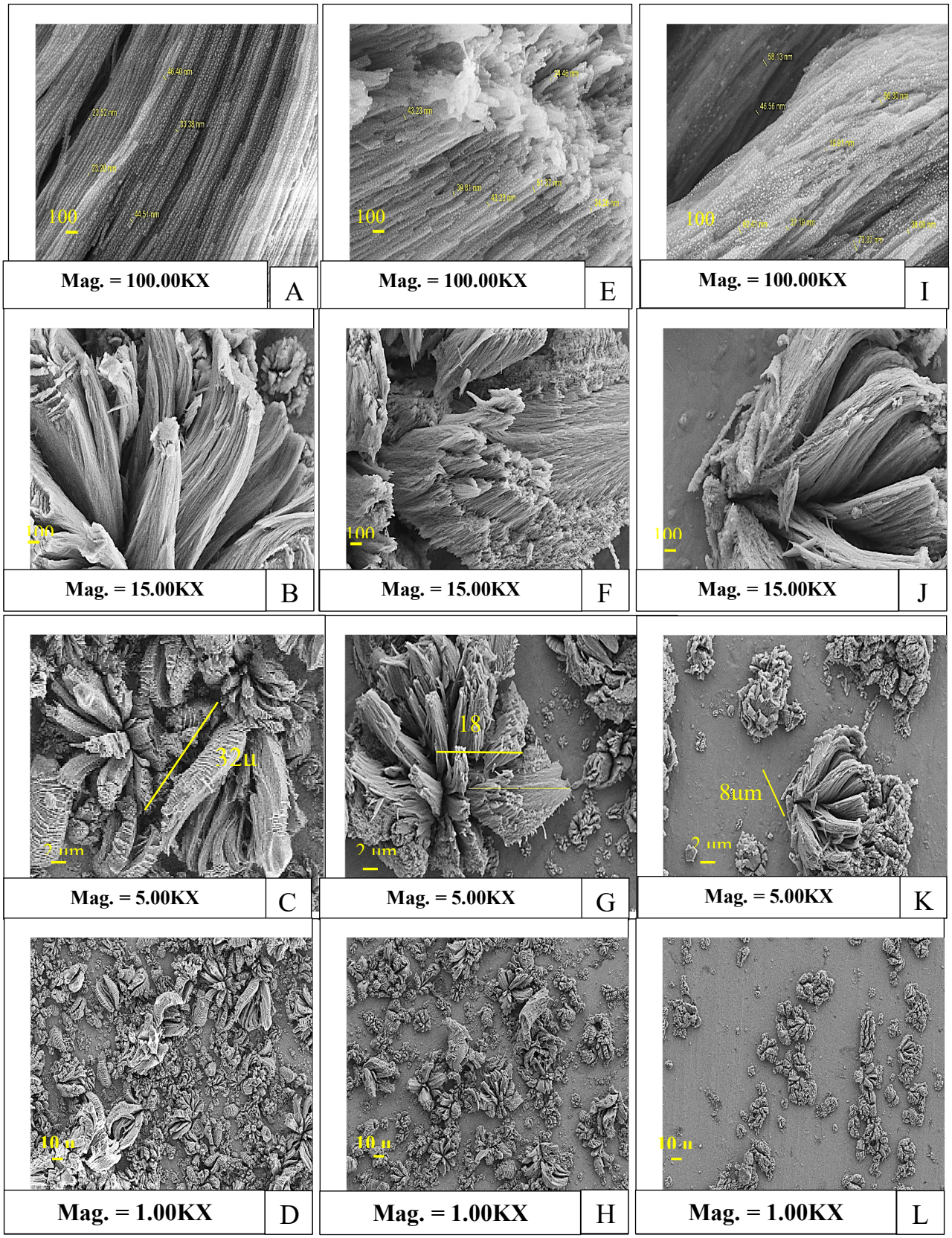

Fig. 1. SEM images of anodized Ti by modified RBA: (A to D) Glycerol 25%; (E to H) Glycerol 50% and (I to L) Glycerol 75%.

SEM images (A, E, and I) in Figure 1 revealed that the TNWs were in the shape of micro bundles. The average nanowire diameter was measured and tabulated in Table 2. This diameter increased with the glycerol volume ratio. Also, Figure 1 shows that; the increase in glycerol did not change the shape of the nanowires but the nanowires' tallest length reduces from 32µm to 8µm, see images C,G, and K. This result is in agreement with the reports that confirmed that the use of glycerol produced long TNTs due to its high relative viscosity (Zainovia *et al*. 2011).

Table2. Variation of TNWs dimensions with Glycerol volume ratio.

	Glycerol 25%	Glycerol 50%	Glycerol 75%
Nanowires' tallest length	32 µm	18 µm	8 µm
Average Nanowire diameter	36.8nm	39nm	46.8 nm

It can be noticed from the SEM images and optical micrographs (Figure 2) that there are areas free from the effects of anodizing, where the bundle structure is absent from those areas, which indicates that the anodizing process may have attacked only areas containing stresses or weak areas. Increasing glycerol increases the viscosity of the anodizing solution, which affects the movement of ions and thus weakens the process of effective ions attacking the weak sites on the surface of the titanium (Lim *et al*., 2016).

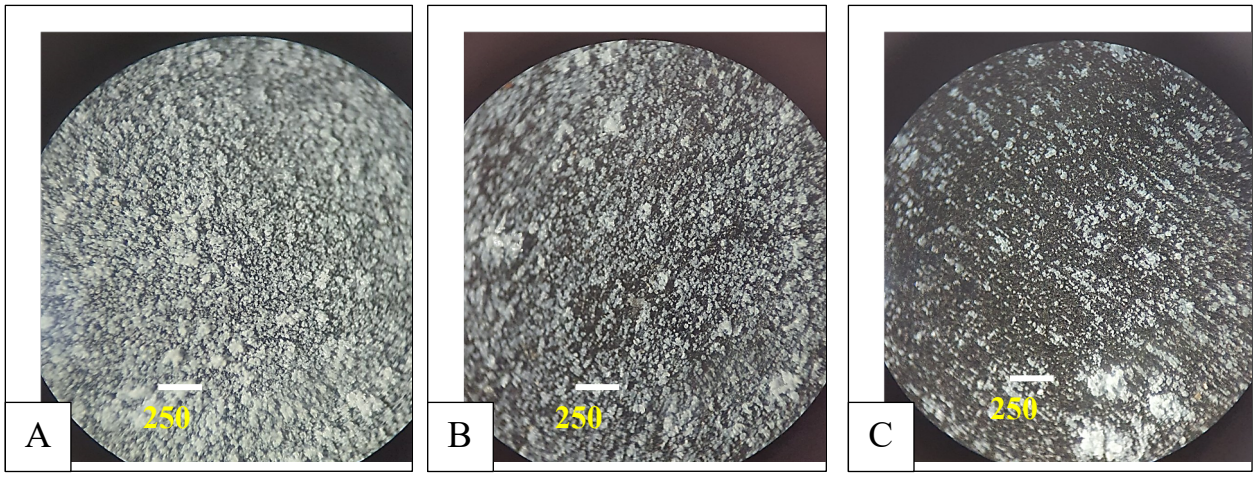

Fig. 2. Optical micrographs for as prepared samples A: Glycerol 25%; B: Glycerol 50%;C: Glycerol 75%.

The atomic compositions that make up the TNWs are shown in EDX spectra in Figure 3; wt% and at% of these elements are tabulated in Table 3.

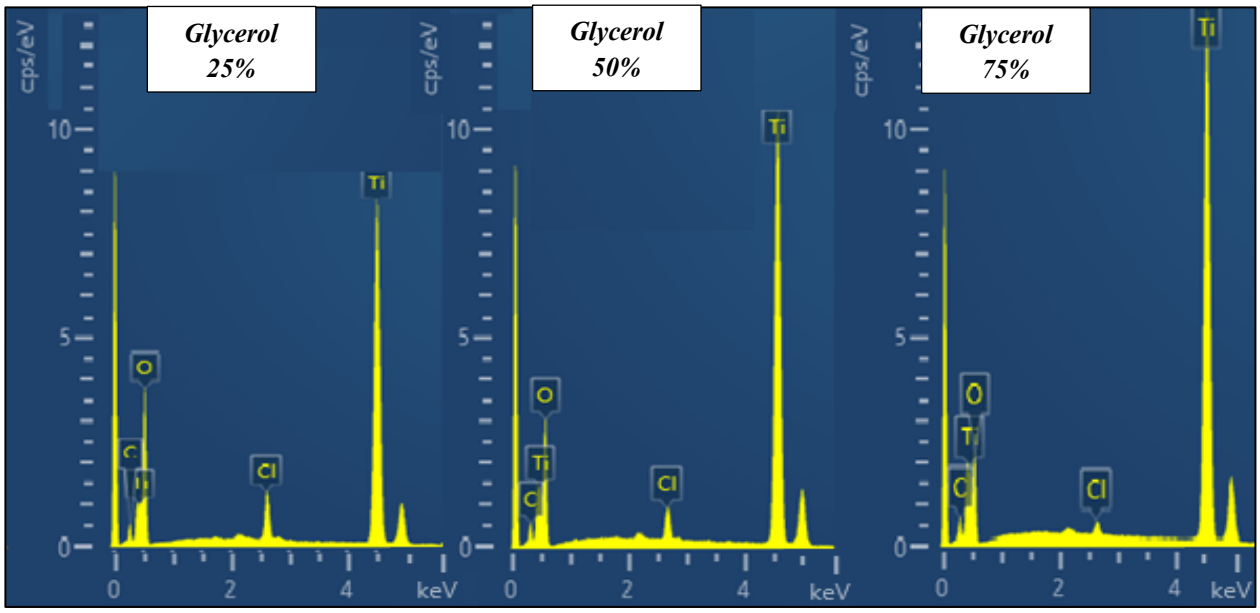

Fig. 3. EDX patterns of the three samples with different glycerol ratio.

Table 3. Weight% and Atomic% for the TNWs elements.

Element	Glycerol 25%		Glycerol 50%		Glycerol 75%	
	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%
Ti	46.3	22.3	54.5	28.3	63.4	36
O	46.2	66.7	39.3	61.2	31.1	52.9
C	4.8	9.2	4.4	9.2	4.6	10.4
Cl	2.63	1.71	1.71	1.2	0.75	0.58
	100.00	100.00	100.00	100.00	100.00	100.00

After anodizing, the presence of oxygen in the Table3 confirmed the oxide production. Observing the Ti/O ratio in this Table shows that it varies with glycerol ratios. The anodized sample with the highest percentage of oxygen had the lowest percentage of glycerol; this clearly indicates the effective role of glycerol in reducing the oxidation process and then forming titanium oxides.

At about 0.2 keV, an extra peak of the C element was identified in the EDX spectra. This element was formed as a result of the glycerol electrolyte that was absorbed by the TNWs during the electrochemical process.

EDX spectra show peaks belonging to chlorine indicating its entry into the structure of TNWs. The source of this element is perchloric acid, which was used in the anodizing solution. Table 3 shows the inverse relationship between the amount of glycerol and the chlorine element, this is a natural result of the materials' percentages used in the anodizing solution for this work.

Figure 4 shows the XRD patterns of the three samples. There are no peaks associated with the titanium oxides, which refers to the amorphous structures of these two phases. All the peaks in these patterns correspond to the pure titanium phase. The intensity of the dominant peak (103) increased when the glycerol percentage was increased from 25% to 75%. The coexistence of titanium oxide amorphous phase with Ti crystalline phase may explain the changes in these patterns.

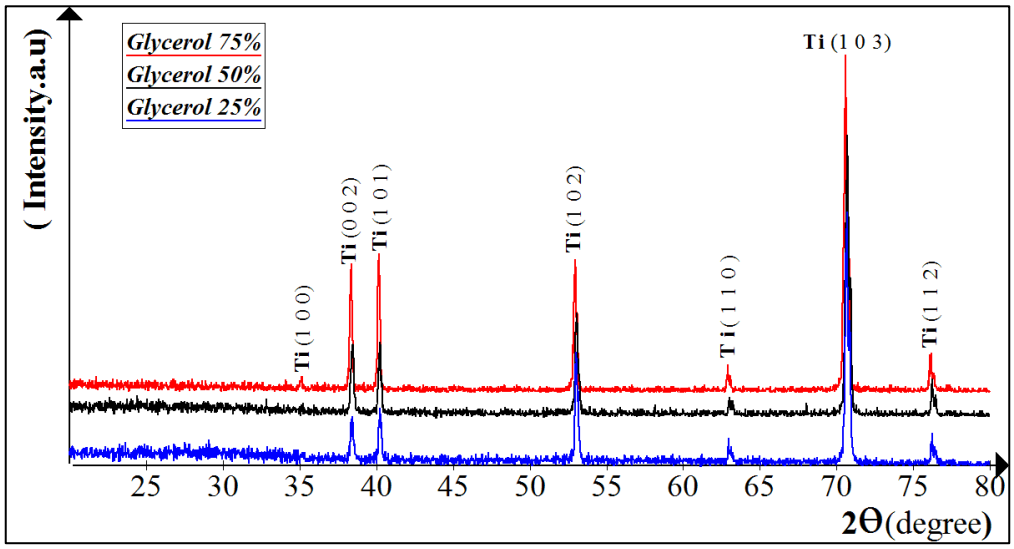

Fig. 4. XRD patterns of as prepared samples by modified RBA technique.

3.1Mechanism formation of TNWs

The process of the formation of TNWs includes three main steps: oxidation of the Ti surface, etching of the oxidation layer, and building nanowires. After the electrochemical cell's power is turned on, metallic cations (Ti^{4+}) form on the anode's surface:

$$Ti \rightarrow Ti^{4+} + 4e^{-} \quad (1)$$

As shown in eq.2, TiO_2 begins to form on the Ti metal's surface, with O^{2-} species arising from H_2O dissociation (Su *et al*. 2016).

$$Ti^{4+} + 2O^{2-} \rightarrow TiO_2 \quad (2)$$

After the formation of the titania starting layer, the electric field inside this layer controls the Ti^{4+} outward migration and the O^{2-}inward movement (Taib *et al*. 2016). Because of this migration, the volume of TiO_2 increased, and the lattice distortion increased. To minimize internal stress, a considerable number of microcracks occur at the oxide/electrolyte contact. The electrolyte instantly fills these gaps.

Chemical etching happens when chloride ions are present, causing cracks to grow bigger and turn into pits. Cl^- ions can also be incorporated into the TiO_2 lattice, see eq. 3.

$$TiO_2 + 6Cl^- + 4H^+ \rightarrow [TiCl_6]^{2-} + 2H_2O \quad (3)$$

The oxide layer is formed within the pits as O_2 ions transfer inward from the electrolyte to the metal surface after pitting. The oxidized metal ions Ti^{4+} move outwards, and the Titanium oxide layer that forms is peeled away by the chloride ions, resulting in water soluble $[TiCl_6]^{2-}$ ions.

When the balance between oxide growth and chemical etching of oxide is maintained, TNWs are generated (Saima *et al*.2018).

Figure 5 demonstrates the formation of TNWs from nanoparticles with size less than 10 nm, indicating that these particles were created first and then rejoined in the form of nanowires.

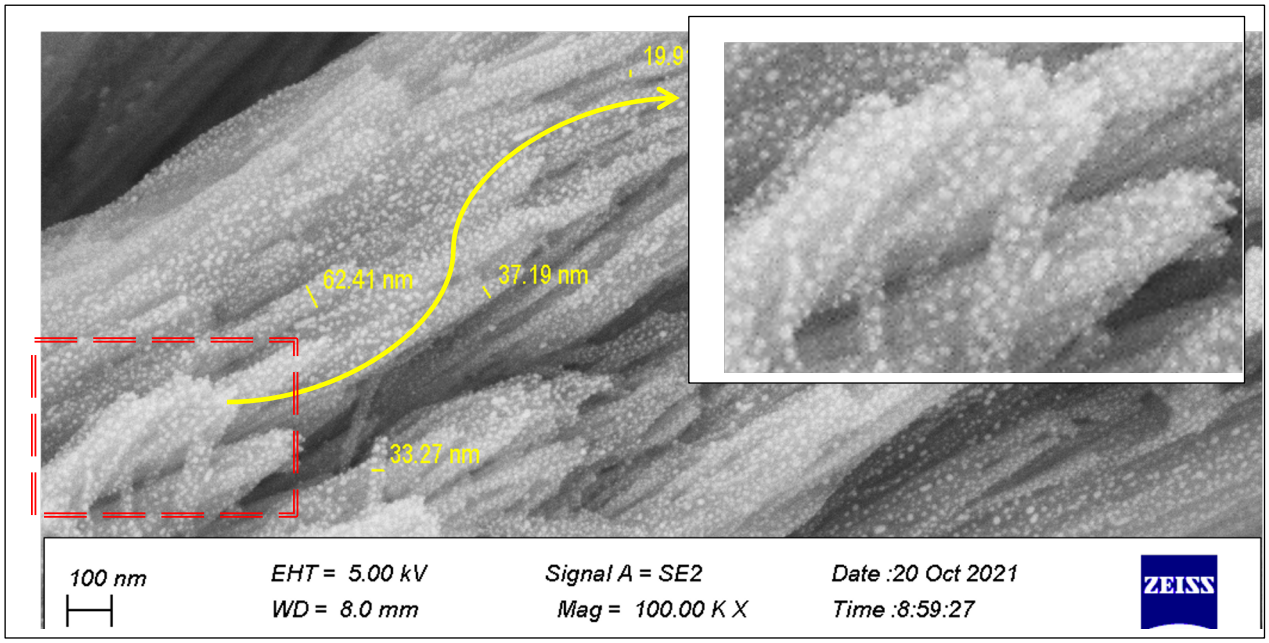

Fig. 5. The formation of TNWs from TNPs.

By comparing the RBA process (without glycerol), which produces TNTs in powder form (Rajini *et al*., 2011), with the current process of producing TNWs in the presence of glycerol; one found that the separation of TNWs from Ti base into chemical solution stopped and the construction process of TNWs was enhanced. The inseparability of TNWs may be attributed to the reduction of the tensions between them and the Ti base as a result of the presence of glycerol (Fahim *et al*., 2009). Also, the gases arising from the reactions may separate TNWs from Ti base, but the presence of the high density of glycerol slowed the rate of these gases.

3.2 The role of the electric field during TNWs forming

The electric field between the cathode and the anode affects the RBA process and the construction of TNWs because it affects the ions exchanged during this process. Image D, H, and L in Figure.1 shows that some areas of the Ti base are free of TNWs, which could be attributed to a weaker electric field in those locations and a stronger electric field in others. The presence of strong electric field regions is due to the presence of nano protrusions on these locations, which make them more susceptible to anodizing reactions than others, resulting in the formation of nano bundles only on these locations (Mustafa & Reem, 2018). Therefore, it can be concluded that the number of nano-protrusions decreases in the presence of glycerol because it reduces the stresses that produced them.

Image A, E, and I in Figure.1 show the parallelism of the nanowires to each other, which indicates the effect left by the electric field. As for the curvatures of these wires, they may have resulted from the drying out and evaporation of the water of the chemical anodizing solution.

Finally, one of the properties of the TNWs produced in this research, as shown in Figure.1, is that they adhere to each other and do not exist individually. This connection process may lower the surface energy of TNWs (Sweta *et al*.2020).

4.Conclusions

The anodizing method can be effective for producing TNWs and controlling the dimensions of these nanostructures using a suitable electrolyte solution. The amount of glycerol in the anodizing solution did not affect the overall shape of TNWs, but it could change their lengths and diameters.

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