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(54) **METHOD OF PREPARATION OF HEXAGONAL TiO₂ NANOTUBES ON TITANIUM SUBSTRATE**

(57) The present invention relates to a method for producing hexagonal TiO₂ nanotubes on a titanium substrate using an anodic oxidation process in the presence of a chelating agent and ultrasound, wherein the anodic oxidation process is carried out: in a two-electrode system, where the working electrode is a titanium foil, preferably 99.7% pure and 0.25 mm thick, and the reference electrode is a platinum foil, preferably 99.95% pure and

0.05 mm thick; in a single step at a constant anodising voltage in the range 10 to 100 V, preferably 20 to 80 V; in the presence of ultrasound with a frequency of 45 kHz and a power of 200 W; in an electrolyte containing: 90-97.5% ethylene glycol, 2.5-10% deionised water, 0.1-0.5% by weight of ammonium fluoride, and 0.09% by weight of disodium edetate Na₂[H₂EDTA]; between 10 and 180 minutes, preferably between 40 and 90 minutes.

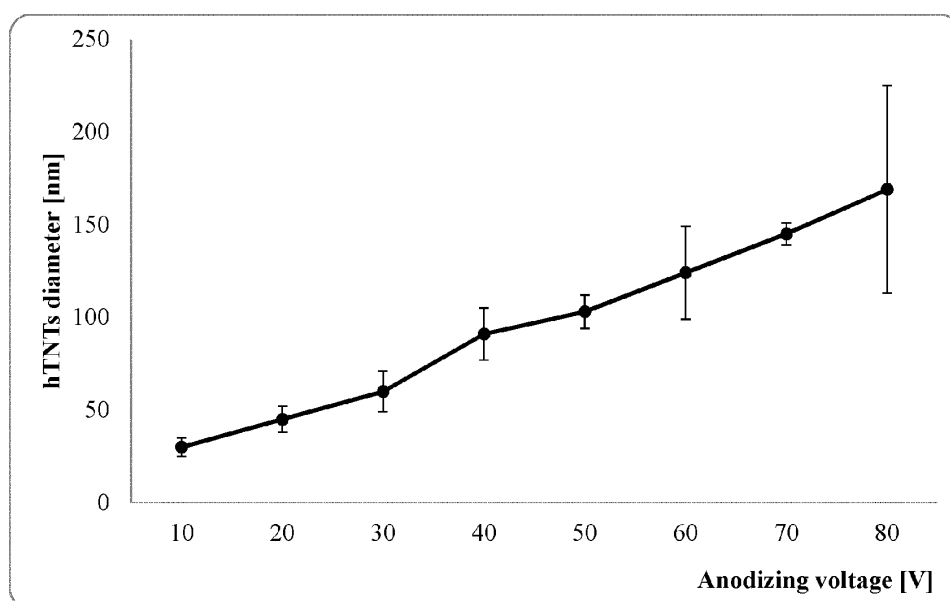


Fig. 1

Description

[0001] The present invention relates to a method for producing hexagonal TiO_2 nanotubes on a titanium substrate.

State of the art

[0002] US patent application US2010269894A1 discloses a method in which a titanium substrate is anodised to form an array of titanium dioxide nanotubes on the surface of the substrate. The nanotubes have a hexagonal pore structure, are inherently hexagonal along their length and are tightly packed. The electrolyte solution used in the anodising process contains the complexing agent $\text{Na}_2[\text{H}_2\text{EDTA}]$. Titanium dioxide nanotubes are formed at a rate of approximately $40 \mu\text{m/hr}$. The titanium dioxide nanotube array is detached from the substrate, leaving the array at room temperature or applying heat to the array. The resulting titanium dioxide membrane has a barrier layer on the back side of the membrane that encloses one end of the constituent nanotubes. The barrier layer can be removed by chemical etching to form a membrane containing nanotubes with open ends. The document discloses conducting the process at a voltage of at least 80 V.

[0003] International patent application WO2021093785A1 discloses a method for producing TiO_2 nanotubes, which have a circular shape and only the form of their arrangement is hexagonal. Furthermore, in this solution, anodisation is carried out in two stages.

[0004] Chinese patent application CN112156202A discloses a method for producing TiO_2 nanotubes, which have a circular shape, their alignment form is hexagonal and the resulting layer is highly heterogeneous.

[0005] Chinese patent application CN102191529A discloses a method for producing TiO_2 nanotubes, which have a circular shape and the form of their arrangement is hexagonal.

[0006] The aim of the present invention was to develop a method of producing hexagonal TiO_2 nanotubes on a titanium substrate that allows the diameter (circle circumscribed about a regular hexagon) of the hexagonal titanium dioxide nanotubes, as well as the height of the resulting nanotubes, to be effectively adjusted by simply changing the process conditions.

[0007] This was achieved by a method of producing hexagonal TiO_2 nanotubes on a titanium substrate according to the present invention.

[0008] Thus, the subject matter of the present invention is a method for producing hexagonal TiO_2 nanotubes on a titanium substrate using an anodic oxidation process in the presence of a chelating agent and ultrasound, wherein the anodic oxidation process is carried out: in a two-electrode system, where the working electrode is a titanium foil, preferably 99.7% pure and 0.25 mm thick, and the reference electrode is a platinum foil, preferably 99.95% pure and 0.05 mm thick; in a single step at a

constant anodising voltage in the range 10 to 100 V, preferably 20 to 80 V; in the presence of ultrasound with a frequency of 45 kHz and a power of 200 W; in an electrolyte containing: 90-97.5% ethylene glycol, 2.5-10% deionised water, 0.1-0.5% by weight of ammonium fluoride, and 0.09% by weight of disodium edetate $\text{Na}_2[\text{H}_2\text{EDTA}]$; between 10 and 180 minutes, preferably between 40 and 90 minutes.

[0009] The beneficial effects of the present invention are shown in the figures of the drawing, where:

Fig. 1 shows the relation of the diameter of hexagonal titanium dioxide nanotubes on anodising voltage;

Fig. 2 shows the relation of the height of hexagonal titanium dioxide nanotubes on anodising voltage;

Fig. 3 shows the relation of the diameter of hexagonal titanium dioxide nanotubes on ethylene glycol concentration at anodising voltages of 20, 50 and 80 V;

Fig. 4 shows the relation of the height of hexagonal titanium dioxide nanotubes on ethylene glycol concentration at anodising voltages of 20, 50 and 80 V;

Fig. 5 shows the relation of the diameter of hexagonal titanium dioxide nanotubes on the fluoride ion concentration at anodising voltages of 20, 50 and 80 V;

Fig. 6 shows the height relation of hexagonal titanium dioxide nanotubes on fluoride ion concentration at anodising voltages of 20, 50 and 80 V;

Fig. 7 shows the relation of the diameter of hexagonal titanium dioxide nanotubes on anodising time at an anodising voltage of 50 V.

EXAMPLES

[0010] Sonochemical-assisted chelating agent-controlled anodisation was performed to produce a layer of hexagonal titanium dioxide nanotubes (hTNTs) on a titanium substrate. The anodisation was performed in a two-electrode system, where the working electrode was a titanium foil of 99.7% purity and 0.25 mm thickness, and the reference electrode was a platinum foil of $25 \times 25 \times 0.05$ mm and 99.95% purity - foils purchased from Sigma-Aldrich. The titanium foil was cut into $20 \times 5 \times 0.25$ mm samples and then subjected to cleaning in acetone and distilled water for 10 minutes each, respectively, in a 300 W ultrasonic cleaner. After cleaning, the titanium substrates were dried in a stream of nitrogen. A STAMOS S-LS-100 laboratory power supply unit was used for anodising. The anodising processes were carried out in a single step under potentiostatic conditions using ultrasound generated by a VWR. USC-T ultrasonic cleaner with an ultrasound frequency of 45 kHz and a power of 200 W. The 100 ml electrolyte consisted of ethylene gly-

col with ammonium fluoride and disodium edetate. A field emission scanning microscope (FESEM, JEOL JSM-7600F) was used to study the morphology of the hTNTs produced, whereby the diameter and height values were determined and the production of hTNTs was confirmed by anodising with the set parameters.

[0011] The anodising time and voltage, as well as the ethylene glycol concentration, were determined as controlling parameters for the diameter and height values of the hTNTs produced by anodising. In addition, the effect of fluoride ion concentration from ammonium fluoride was analysed.

1a. The anodising voltage was varied in the range 10-80 V, time 60 minutes, sonication at 45 kHz and electrolyte composition: 95% ethylene glycol, 0.30% by weight NH_4F and 0.09% by weight $\text{Na}_2[\text{H}_2\text{EDTA}]$. Fig. 1 shows the relation of the diameter of the hexagonal titanium dioxide nanotubes on the anodising voltage, while Fig. 2 shows the relation of the height of the hexagonal titanium dioxide nanotubes on the anodising voltage.

1b. The effect of ethylene glycol concentration on the diameter and height values of the hTNTs produced was determined for voltages of 20, 50 and 80 V. The samples were anodised for 60 minutes in an electrolyte containing **90.0-97.5% ethylene glycol**, 0.30 wt% NH_4F and 0.09 wt% $\text{Na}_2[\text{H}_2\text{EDTA}]$ with ultrasound. Fig. 3 shows the relation of the diameter of hexagonal titanium dioxide nanotubes on ethylene glycol concentration at anodisation voltages of 20, 50 and 80 V, and Fig. 4 shows the relation of the height of hexagonal titanium dioxide nanotubes on ethylene glycol concentration at anodisation voltages of 20, 50 and 80 V.

1c. The fluoride ion concentration range was chosen as 0.1-0.5 wt% ammonium fluoride concentration in the electrolyte used for anodising. The anodisation was carried out for 60 minutes with an electrolyte content of 95% ethylene glycol, 0.09% wt% $\text{Na}_2[\text{H}_2\text{EDTA}]$ and 0.1-0.5% wt% NH_4F , at anodising voltages of 20, 50 and 80 V with ultrasonication. Fig. 5 shows the relation of the diameter of hexagonal titanium dioxide nanotubes on fluoride ion concentration at anodisation voltages of 20, 50 and 80 V, and Fig. 6 shows the relation of the height of hexagonal titanium dioxide nanotubes on fluoride ion concentration at anodisation voltages of 20, 50 and 80 V.

1d. Effect of anodising time on height and diameter values of hTNTs. For the determined formation parameters, which remain constant, a variation of time in the range 10-90 min was made. The other parameters were held constant and were: anodising voltage 50 V, electrolyte composition 95% ethylene glycol, 0.30% wt% NH_4F , 0.09% wt% $\text{Na}_2[\text{H}_2\text{EDTA}]$,

ultrasound contribution. Fig. 7 shows the relation of the diameter of hexagonal titanium dioxide nanotubes on anodising time at 50 V anodising voltage, and Fig. 8 shows the relation of the height of hexagonal titanium dioxide nanotubes on anodising time at 50 V anodising voltage.

[0012] The present invention uses simple electrochemical equipment and low-cost one-step electrochemical anodic oxidation technology to synthesise an ordered matrix of hexagonal titanium dioxide nanotubes with controlled structural parameters such as the diameter of the titanium dioxide nanotubes and the height of the titanium dioxide layer produced. The proposed method is used to produce a titanium dioxide-based nanomaterial with a hexagonal shape, and the structural parameters can be effectively controlled by varying the anodic oxidation voltage and time, as well as the concentrations of ethylene glycol and ammonium fluoride, which are components of the electrolyte used in the anodic oxidation process.

[0013] The implementation of ultrasound directly into the anodic oxidation process has made it possible to produce a matrix of hexagonal titanium dioxide nanotubes with controlled structural parameters in a single anodic oxidation step, thus reducing the fabrication time of hTNTs. At the same time, a large layer height of hTNTs in the range 7471-20933 nm at 50 V is obtained in a short time of 40-90 minutes.

[0014] The electrolyte used for anodic oxidation contains the following components: 0.1-0.5% by weight of ammonium fluoride, 2.5-10% deionised water, 90-97.5% ethylene glycol and 0.09% by weight of disodium edetate.

[0015] The anodic oxidation process takes place in a single step, during which the pure titanium substrate is anodised at 10-80 V for 40-90 minutes with ultrasound.

[0016] Prior to anodising, the surface of the high-purity titanium substrate was ultrasonically treated successively in acetone and distilled water for 10 minutes.

[0017] The anodising device uses a two-electrode system, where the cathode is platinum sheet and the anode is pure titanium. The area of pure titanium exposed to the electrolyte is a 5x5 mm square area and the distance between the electrodes is 21 mm.

Claims

1. A method for producing hexagonal TiO_2 nanotubes on a titanium substrate using an anodic oxidation process in the presence of a chelating agent and ultrasound, wherein the anodic oxidation process is carried out:

- in a two-electrode system, where the working electrode is a titanium foil, preferably 99.7% pure and 0.25 mm thick, and the reference electrode is a platinum foil, preferably 99.95% pure and 0.05 mm thick;

- in a single step at a constant anodising voltage in the range 10 to 100 V, preferably 20 to 80 V;
- in the presence of ultrasound with a frequency of 45 kHz and a power of 200 W;
- in an electrolyte containing:

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90-97.5% ethylene glycol,
 2.5-10% deionised water,
 0.1-0.5% by weight of ammonium fluoride,
 and
 0.09% by weight of disodium edetate
 $\text{Na}_2[\text{H}_2\text{EDTA}]$;

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- between 10 and 180 minutes, preferably between 40 and 90 minutes.

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2. The method according to claim 1, **characterised in that**, prior to the anodising process, the titanium foil is cleaned successively in acetone and distilled water for 10 minutes in a 300 W ultrasonic cleaner, and then the cleaned titanium foil is dried in a stream of nitrogen. 20
3. The method according to claim 1 or 2, **characterised in that** the ammonium fluoride content in the electrolyte is from 0.20 to 0.40% by weight, preferably from 0.25 to 0.35% by weight. 25
4. The method according to claim 1 or 2 or 3, **characterised in that** the anodic oxidation process is carried out at a time from 10 to 180 minutes, preferably between 40 and 90 minutes. 30
5. The method according to any of the claims 1-4, **characterised in that** the distance between the electrodes is between 18 and 22 mm, preferably 21 mm. 35
6. The method according to any of the claims 1-5, **characterised in that** the anodic oxidation process is carried out at room temperature. 40

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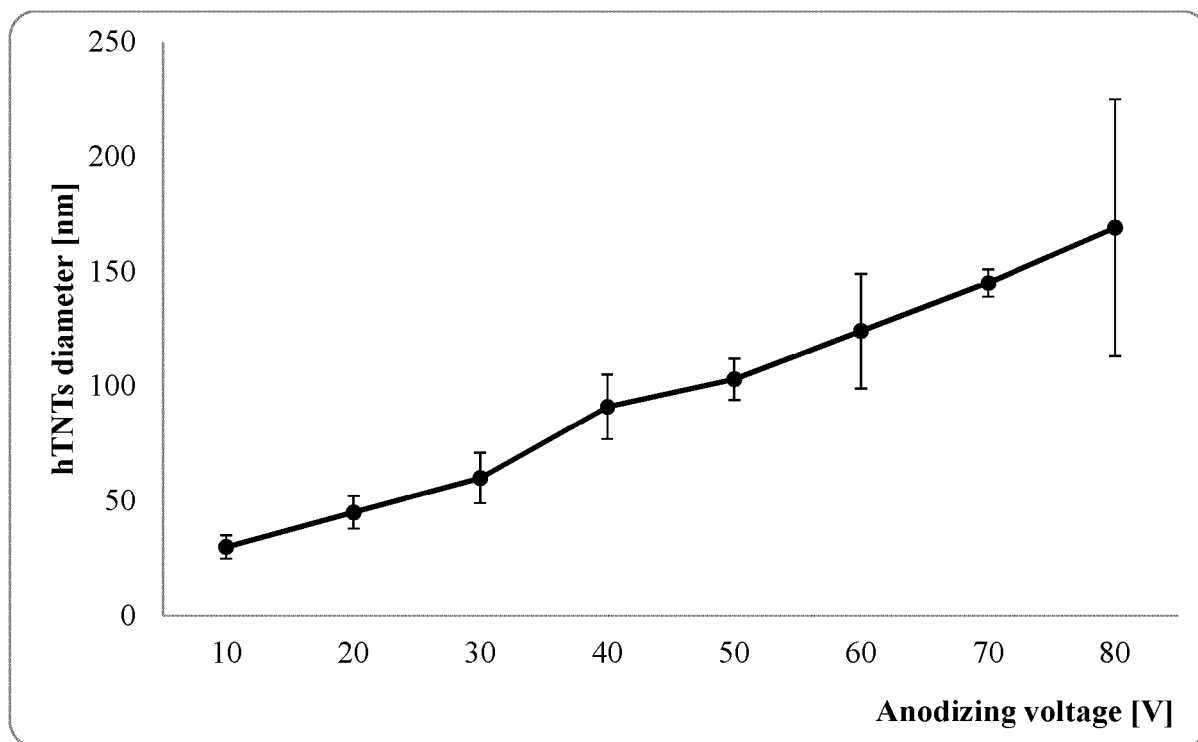


Fig. 1

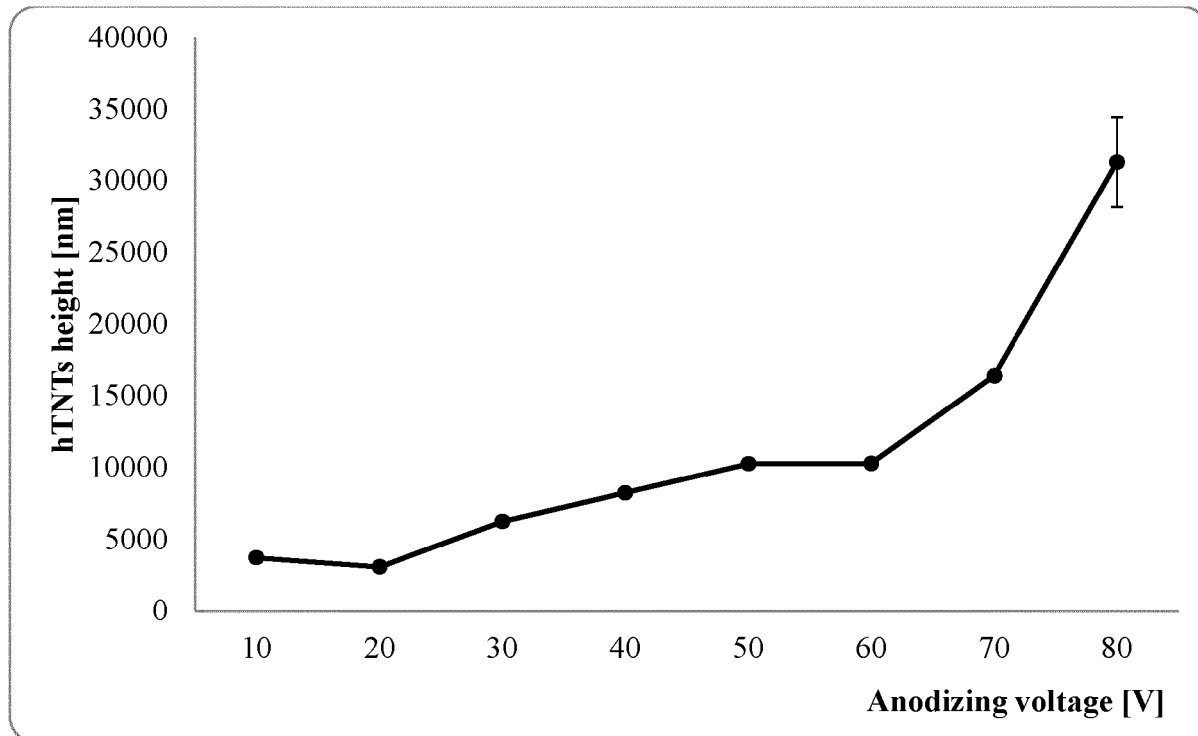


Fig. 2

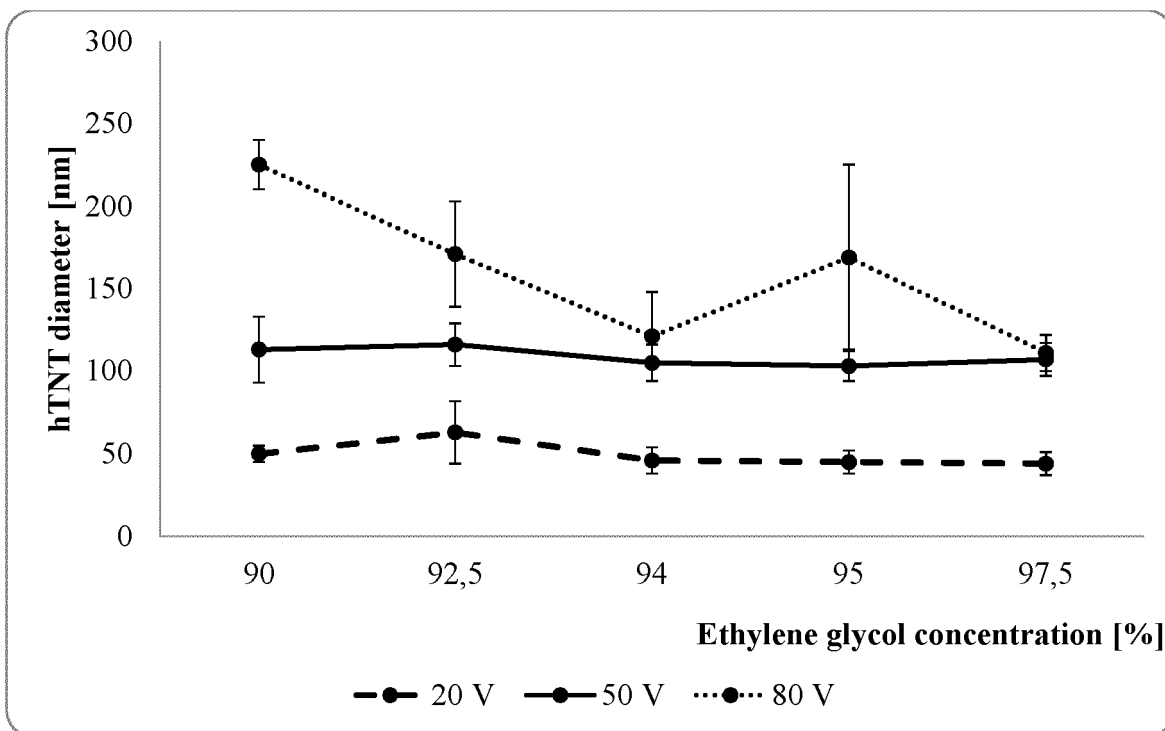


Fig. 3

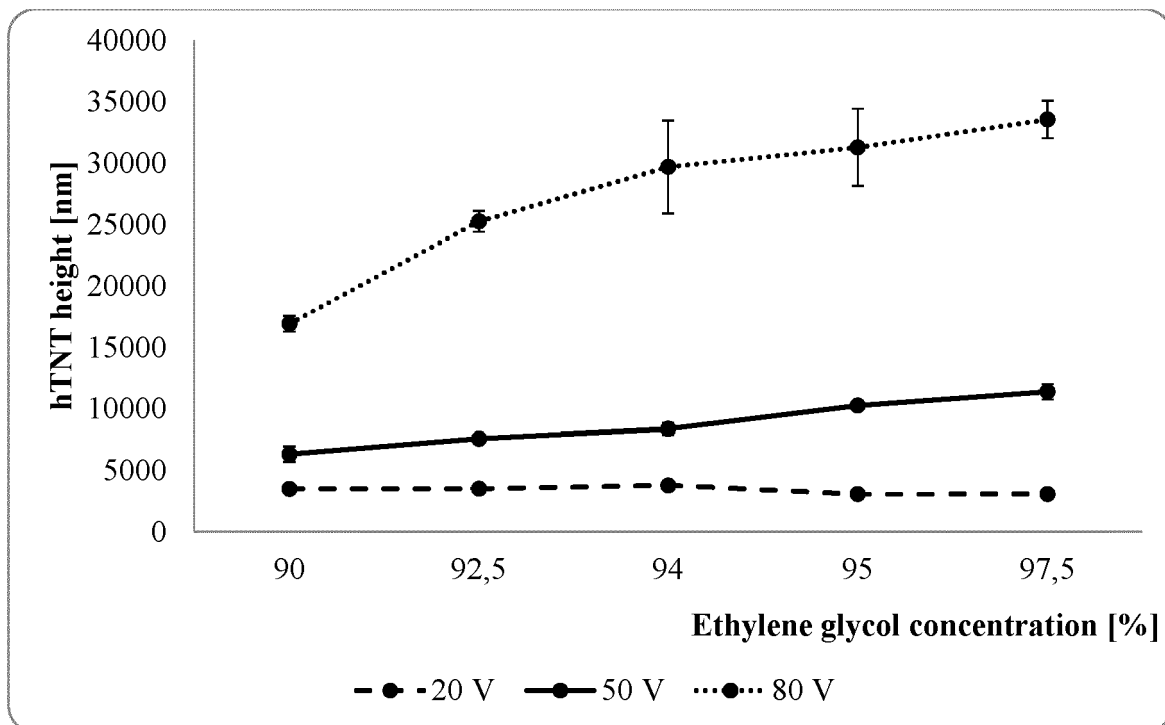


Fig. 4

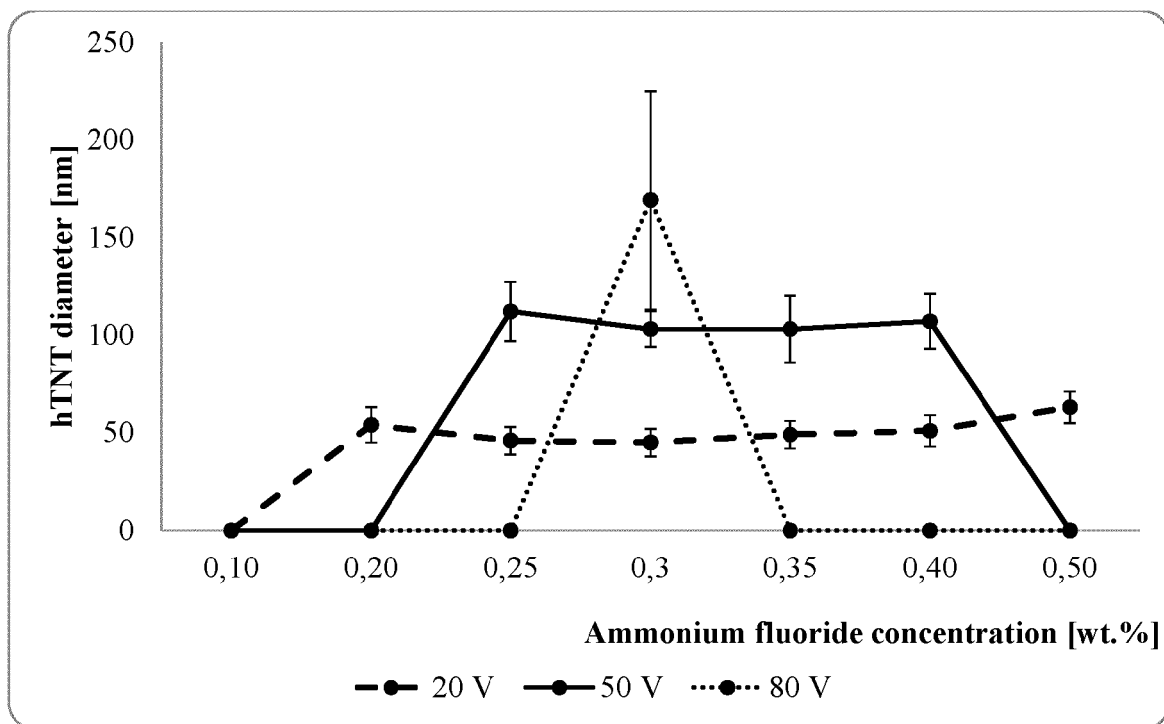


Fig. 5

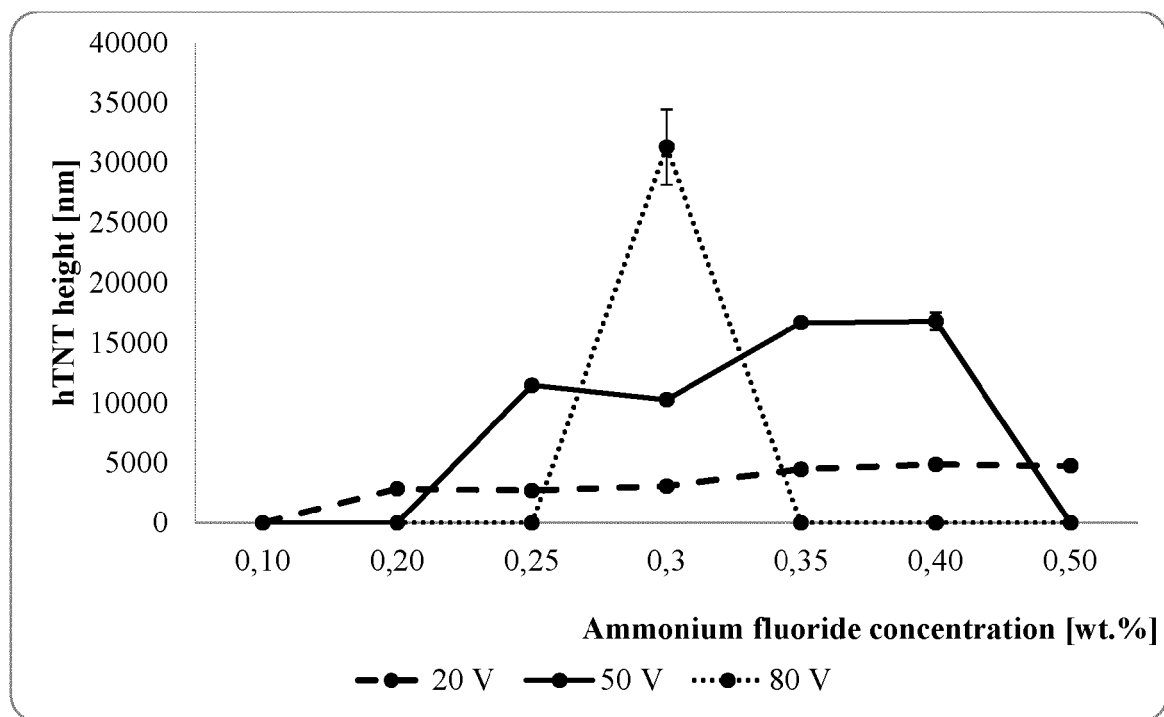


Fig. 6

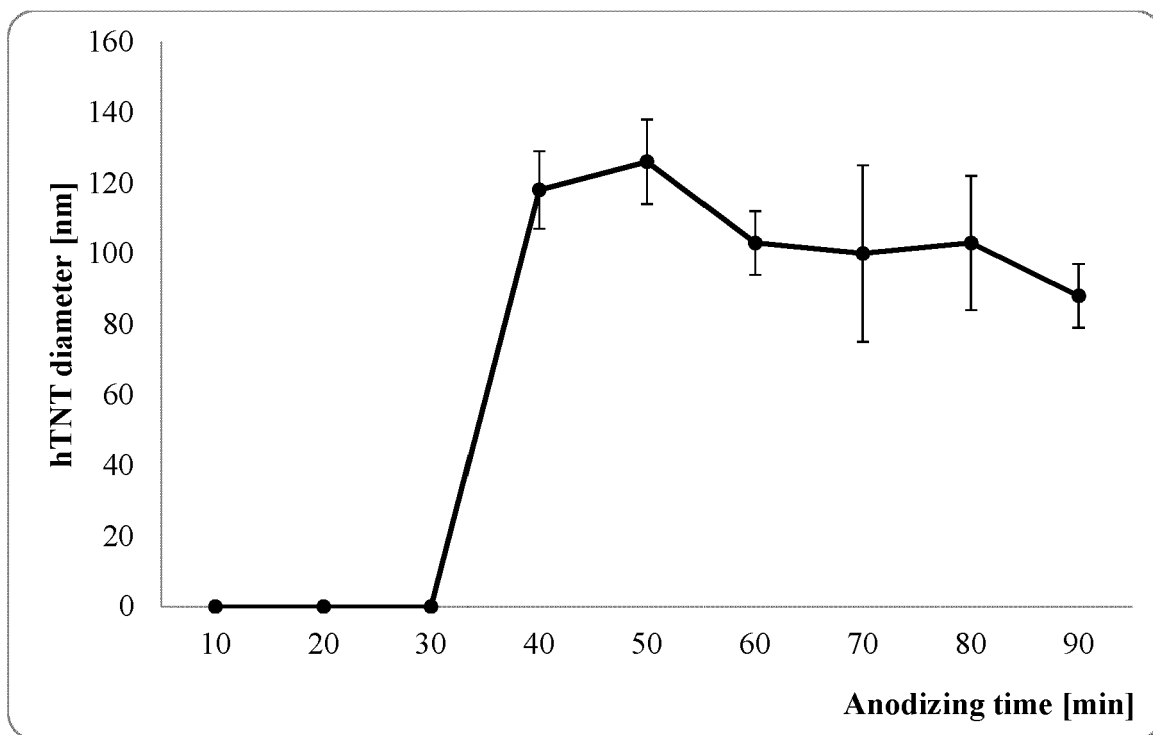


Fig. 7

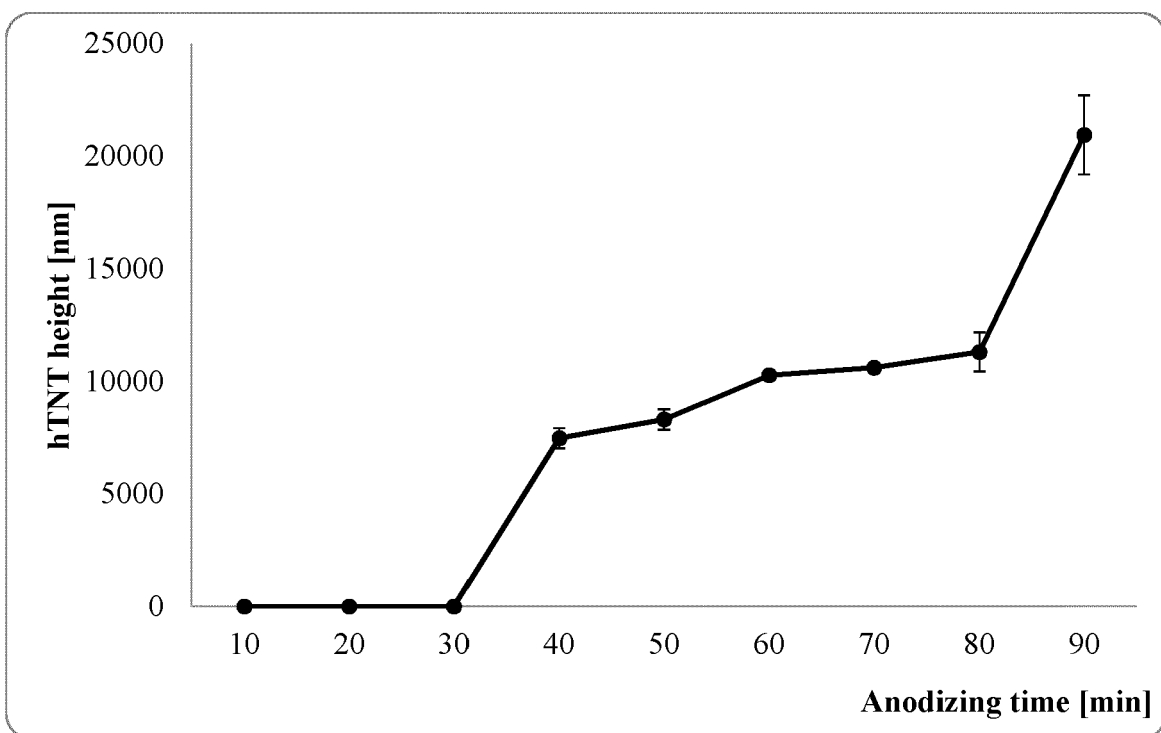


Fig. 8



EUROPEAN SEARCH REPORT

Application Number

EP 23 46 1585

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EPO FORM 1503 03.82 (P04C01)

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
Y, D	US 2010/269894 A1 (MISRA MANORANJAN [US] ET AL) 28 October 2010 (2010-10-28) * paragraph [0072] * * paragraph [0086] - paragraph [0088] * -----	1-6	INV. C25D11/26
Y	US 2010/320089 A1 (MISRA MANORANJAN [US] ET AL) 23 December 2010 (2010-12-23) * paragraph [0002] * * paragraph [0038] * * paragraph [0041] - paragraph [0044] * * paragraph [0048] * * paragraph [0051] * * paragraph [0075] * -----	1-6	
Y	PEIGHAMBARDOUST NAEIMEH-SADAT ET AL: "Improved performance of anodic titanium oxide nanotube arrays synthesized by sonoelectrochemical anodization method for dye-sensitized solar cells", APPLIED PHYSICS A, SPRINGER BERLIN HEIDELBERG, BERLIN/HEIDELBERG, vol. 123, no. 5, 12 April 2017 (2017-04-12), pages 1-10, XP036240760, ISSN: 0947-8396, DOI: 10.1007/S00339-017-0925-2 [retrieved on 2017-04-12] * Abstract Experimental procedure * -----	2	TECHNICAL FIELDS SEARCHED (IPC) C25D
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 9 October 2023	Examiner Telias, Gabriela
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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EP 23 46 1585

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09-10-2023

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2010269894 A1	28-10-2010	NONE	
US 2010320089 A1	23-12-2010	EP 2121184 A2	25-11-2009
		US 2010320089 A1	23-12-2010
		WO 2008073968 A2	19-06-2008

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- US 2010269894 A1 **[0002]**
- WO 2021093785 A1 **[0003]**
- CN 112156202 A **[0004]**
- CN 102191529 A **[0005]**