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STRUCTURE, MORPHOLOGY AND PHASE COMPOSITION OF ANODIZED TITANIUM DIOXIDE NANOTUBES LOADED WITH Pt AND Pd

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This study focuses on titanium dioxide (TiO_2) nanotubes on solid substrates, which may find wide applications as photocatalysts and catalysts. To address the need for more stable and active electrocatalysts with reduced noble metal content, the study explores Ti_nO_{2n-1} suboxides as promising substrates for the electrocatalysts. Notably, the addition of water in the fluoride-containing electrolyte plays a critical role in shaping the morphology of TiO_2 nanotubes, leading to the formation of ordered structures under specific water concentration conditions. The study also examines the effects of platinum and palladium deposition on TiO_2 nanotubes, enhancing their surface crystallinity and structural arrangement. The presence of an unidentified phase, possibly titanium hydride, is observed in certain samples. The findings highlight the potential of TiO_2 nanotubes as efficient electrocatalysts and the influence of water content and substrate choice on their properties, opening up new avenues for advanced applications in various fields.

Keywords: titanium dioxide nanotubes, morphology, electrodeposition, phase composition, mesoporous structure.

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Introduction

Titanium dioxide films on solid substrates are widely used as photocatalysts [1], gas sensors [2], solar cells [3], ceramic membranes, anti-corrosion and self-cleaning coatings, for enzyme immobilization in medicine [4], etc. At the same time, the mentioned materials seem unsuitable for electrocatalysis due to very low electric conductivity. Titanium suboxides Ti_nO_{2n-1} are considered promising materials to be used as the substrate for the electrocatalyst of the oxygen evolution reaction. They exhibit high electronic conductivity and corrosion resistance in acidic environments and at high anodic potentials [5]. Magnelli phase titania known under the registered trade name Ebonex (Atraverda, Inc., UK) is a subject of particular interest. Ebonex is a nonstoichiometric mixture of titanium oxides with general formula Ti_nO_{2n-1}, where $4 \le n \le 10$. This material has a unique combination of electrical conductivity approaching that of a metal ($\approx 1 \cdot 10^3$ Ω^{-1} cm^{-1}) and high corrosion resistance both in acid and basic solutions [6]. Its chemical composition and hypo-d-electron character suggest an ability to interact with hyper-d-electron metals such as Pt, Ni, Co etc., which is a prerequisite for synergism and increase of catalytic activity [7].

The oxygen evolution reaction occurs under particularly harsh conditions of high anodic potentials, leading to the degradation of conventionally used Ir-based electrocatalysts. The stability of such anodic electrocatalysts is often insufficient to ensure the long-term operation of the electrolyzer [8]. Additionally, the voltage of the electrolysis process largely depends on the overpotential of the anodic oxygen evolution reaction. Therefore, the development of electrocatalysts with high activity and stability, containing significantly reduced amounts of noble metals, is a crucial task. One promising approach to reduce the loading and simultaneously increase the utilization of noble metals is the use of a substrate that should be accessible, stable under the mentioned conditions, and possess a high surface area and electronic conductivity.

In this work that can be considered a continuation of a previous published work [9], comprehensive study upon physicochemical properties of materials was carried out by using Pd and Pt loaded TiO_2 metal loaded samples. The loaded TiO_2 anodes

were characterized using XPRD, EDAX, and SEM techniques and the effect of the noble metal (as single or in pairs) on the structure, morphology and phase composition of anodized titanium dioxide nanotubes was studied.

Material and methods

The treatment with emery papers was used to obtain smooth Ti plate surface. The Ti-plates were degreased in 5 M alkali and pickled in 6 M hydrochloric acid for 20 min. The dimensions of the plate were 1.0 cm×1.0 cm×0.10 cm. After each step, the plates were washed in water, and then dried.

The solution was prepared by dissolving NH_4F (0.25 wt.%) in a solution of water and ethylene glycol (2:49, v/v) which was described elsewhere [9]. The cathode was a Pt. The anodic oxidation was performed by immersing the Ti plates at 40 V for 4 h by using a direct current (DC) power supply device in a container of high-density polyethylene. Obtained nanotubes were partially reduced through cathodic polarization, resulting in the formation of titanium suboxides with different stoichiometry. The reduction was conducted in 1 M $HClO_4$ during 1 h. A few pieces of Ti/TiO_2 nanotube anodes were loaded with different noble metals. It should be noted that metals, both platinum and palladium, are not deposited on the surface of unreduced nanotubes. This phenomenon can be explained both by the blocking of the surface by hydroxides and by the low electrical conductivity of titanium dioxide as a semiconductor. If the synthesized nanotubes are reduced, then a layer of metal can be applied electrochemically to pretreated surface. The samples were loaded with Pt and Pd in aqueous solutions of precursors of noble metals. Nitrite electrolyte was used for platinizing and phosphate electrolyte was used for palladization [10]. Depending on the task, the amount of platinum and palladium on the template surface varied from 0.25 to 1.0 mg/cm^2. The same procedures were used for bimetallic loading. The as-formed TiO_2 nanotubes were in the amorphous phase, consequently the plates were calcined in a tube furnace at 500^{0}C (temperature increasing rate of 2^{0}C/min) to transform them into crystalline form. This approach enabled the creation of a porous surface on the matrix for subsequent electrodeposition of catalytic layers of platinum and/or palladium. Subsequent heat treatment under varying partial oxygen pressure allowed for the formation of composites with different compositions. The high concentration of cation vacancies and oxygen ion deficiency in the matrix significantly increased the mobility of platinum/palladium atoms during the heat treatment, resulting in a nearly metallic electrical conductivity of the formed composites. It should be noted that heat treatment at a temperature above 700^{0}C leads to complete sublimation of palladium from the surface [10] Also, at high processing temperatures in air, the formation of titanium nitrides is possible, which will form titanium oxide during anodic polarization [10], that is undesirable in this work.

The prepared electrocatalysts series were observed by SEM microscopy, while the surface composition was determined by means of EDX analysis. For this purpose, SEM-106I microscope was used. XRPD data were collected in the reflection mode on a STOE STADI P diffractometer with the following setup: Cu $K\alpha_1$-radiation, curved Ge(1 1 1) monochromator on primary beam, $2\theta/\omega$-scan, angular range for data collection of 2θ=24.000−116.625 with increment of 0.015, linear position sensitive detector with step of recording of 2θ=0.480 and times per step of 100−200 s, U=40 kV, I=35 mA, and T=290 K. Preliminary data processing and X-ray qualitative phase analysis were performed using STOE WinXPOW and PowderCell program packages. Crystal structures of the phases were refined by the Rietveld method with the program FullProf.2k, applying a pseudo-Voigt profile function and isotropic approximation for the atomic displacement parameters. Microstructural parameters (i.e. size of coherently diffracting domains accepted as average apparent crystallite size D, and average maximum strain ε) were identified by isotropic line broadening analysis using simplified integral breadth methods for (200) reflection of face-centered cubic cells of Pt, Pd.

Results and discussion

Figure 1,a shows a sponge-like array of tubes vertically oriented towards the substrate with an inner diameter of approximately 70 nm. The nanotubes appear to be well-ordered, forming a nanocombed pattern. The resulting coating possesses a mesoporous structure. It is likely that there is incomplete dissolution of dense layers of titanium oxide on the coating's surface, leading to the external surface becoming ribbed.

Changes in water concentration led to an increase in the dissolution rate of the inner surface, which determines the diameter of the formed nanotubes. Increasing the amount of water in the fluoride-containing electrolyte solution reduces the viscosity of the solution and, as a result, facilitates the diffusion of H^+ and F^- ions within the porous structure, enhancing the interaction of fluoride ions with TiO_2 [11,12]. Thus, with a low amount of water in the fluoride-containing electrolyte solution, the high viscosity severely limits the diffusion of H^+ and F^- ions, leading to a low dissolution rate of TiO_2 and the formation of a mesoporous structure. By adding water, the viscosity decreases, and the H+ and F^- ions diffusion improves, leading to the formation of an ordered structure of TiO_2 nanotubes.

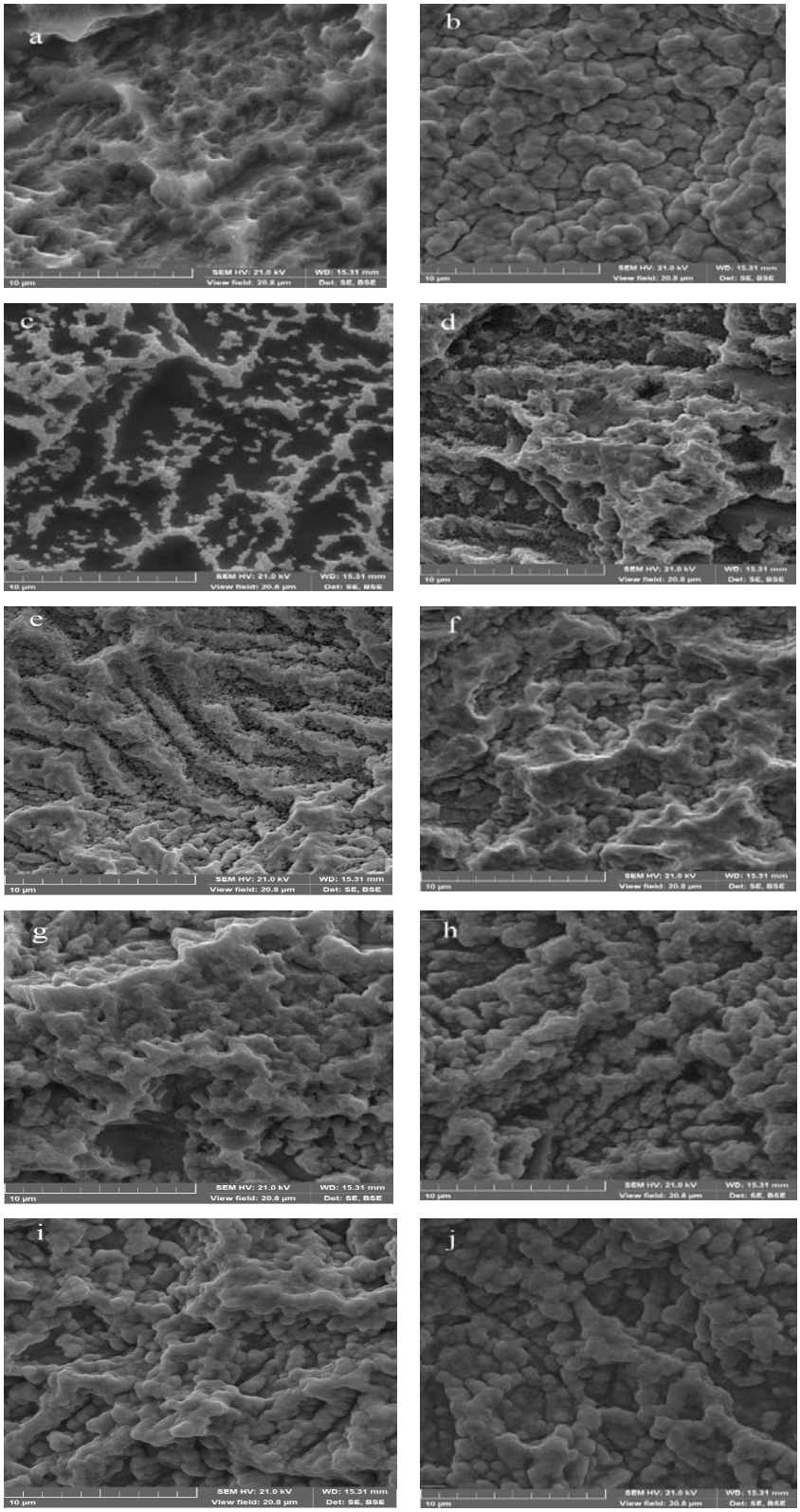

Fig. 1. SEM images of a − naked TiO_2 nanotubes; b − 0.3 mg Pt/0.5 mg Pd loaded TiO_2 nanotubes calcined; c − 0.3 mg Pt loaded TiO_2 nanotubes; d − 0.3 mg Pt loaded TiO_2 nanotubes calcined; e − 0.5 mg Pt loaded TiO_2 nanotubes; f − 0.5 mg Pt loaded TiO_2 nanotubes calcined; g − 0.3 mg Pd loaded TiO_2 nanotubes; h − 0.3 mg Pd loaded TiO_2 nanotubes calcined; i − 0.5 mg Pd loaded TiO_2 nanotubes; and j − 0.5 mg Pd loaded TiO_2 nanotubes calcined electrodes

The amount of water used in the electrolyte in this study leads to the formation of highly organized films composed of densely packed arrays of TiO_2 nanotubes with a narrow size distribution. As noted by Valota et al. [13], within the range of water content in the electrolyte from 0.5 to 4%, the formation of nanotubes with a smooth external surface is observed.

The plate surface is densely covered with Pt nanoparticles (Fig. 1,c–f). The particle sizes of Pt metals show a distribution between 1 and 43.5 nm for 0.3 and 1.0 mg load, respectively [9]. Pt nanoparticles appeared clustered on the plate surface. SEM images show that metals form a thin film on the surface rather than exist as Pt nuclei. The higher the metal load, the denser the film on coating surface becomes. TiO_2 nanotubes coated with a thin layer of platinum exhibit a highly developed surface, where platinum, due to diffusion and sintering processes, is distributed across the sample's surface. As a result of the thermal treatment, the crystallinity of the coating is enhanced, indicating an improvement in the structural arrangement of the material.

It can be noticed that Pd particles are well distributed on the surface. However, the size distribution of the particles is heterogeneous as metal nanoparticles of various sizes are present on the plate surface. Pd nanoparticles in this plate are bigger and much less scattered than Pt nanoparticles. Surface shows visible fused blocks (Fig. 1,g–j), which is characteristic of the surface morphology of titanium suboxides, Ebonex® in particular [14]. Surface formed mostly with micro-scaled and less submicron aggregates.

EDX mapping for O, F, Ti, Pt and Pd elements is summarized in Table 1. The results indicate that the distribution of the elements on the plate is quite homogeneous. Generally, the atomic percentage values of noble metals on the samples were much less than those of Ti and O, when metal load is 0.3 mg. The presence of F on the plate surface was also found probably due to the use of small amount of NH_4F in the anode preparation.

XPRD patterns of nanotube structured TiO_2 on the surface of anodes together with phase of Ti plate are shown in Fig. 2. The XPRD peaks at $2\theta=25.58^0$, 38.08^0, 48.08^0, and 54.58^0 can be attributed to anatase TiO_2; those at $2\theta=34.95^0$, 38.25^0, 40.05^0, and 52.90^0 can be ascribed to Ti; those at $2\theta=39.8^0$, 46.2^0, and 67.5^0 can be attributed to Pt, and those at $2\theta=40.1^0$, 46.6^0, and 68.1^0 can be ascribed to Pd. Uncalcined TiO_2 on the plate showed to be amorphous as it did not reveal any XPRD patterns attributable to TiO_2 (Fig. 2), which is consistent with the results obtained earlier [15]. All the anodes calcined at 500^0C show the presence of the anatase phase along. In samples loaded with Pd, palladium exists in metallic form and the oxide form. Pt exists in metallic form in all samples.

The phase composition of the samples involved is given in Table 2. In some samples, unidentified phase was observed (broad reflections at $2\theta\sim35.97^0$, 40.96^0, and 59.26^0). If considering SEM/EDX data, it may be a titanium hydride. The primary particle metals sizes were calculated by using the Scherrer equation. For platinum, the particle size varies from 0.99 to 15.5 nm, whereas it varies from 0.97 to 30.3 nm for palladium.

Conclusions

Before annealing, the obtained nanotubes are X-ray amorphous, meaning they lack a well-defined crystalline structure. After annealing at 500^0C, a crystallization process occurs, transforming the nanotubes from the amorphous phase into the anatase phase. As a result, characteristic reflections of the anatase phase appear in the diffraction pattern. Additionally, clear peaks corresponding to the metallic titanium substrate are observed in the diffraction pattern. In the case of introducing noble metals, reflections of metallic platinum, palladium, and palladium oxide appear.

The water content in ethylene glycol has a significant influence on the morphology of TiO_2

Table 1

Surface chemical composition

Load of metal in TiO_2 nanotube matrix	Phase content, wt.%				
	Ti	O	F	Pt	Pd
naked	63.5	30.5	5.4	–	–
0.3 mg Pt	61.1	22.9	1.6	9.5	–
0.3 mg Pt calcined	59.3	11.1	–	28.8	–
0.5 mg Pt	39.3	–	–	59.2	–
0.5 mg Pt calcined	29.0	–	–	71.0	–
0.3 mg Pd	57.5	4.6	–	–	28.0
0.3 mg Pd calcined	50.1	16.0	–	–	25.6
0.5 mg Pd	38.9	2.9	–	–	58.2
0.5 mg Pd calcined	28.8	15.5	–	–	55.7
0.3 mg Pt/0.5 mg Pd calcined	8.5	6.3	–	37.9	32.8

Table 2

Phase composition of the investigated samples, crystallographic data and microstructural parameters for the phases with fcc structure

Sample description	Phases[1]	Lattice parameter a, Å	Unit cell volume V, Å^3	D, Å / ε
naked NT	Ti[2] UP[3]	–	–	–
0.5 mg/cm^2 Pd	Pd 24±1 wt.% Ti 76±2 wt.%	3.8889(3)	58.813(8)	118 / 0.0082
0.5 mg/cm^2 Pd calcined	Pd 10.0(2) wt.% Ti 62.0(7) wt.% PdO[4] 20.2(2) wt.% TiO_2 ana[5] 7.8(5) wt.%	3.89032(17)	58.878(5)	275 / 0.0035
0.3 mg Pt/0.5 mg Pd calcined	Pt 24.7(9) wt.% Pd 16.3(9) wt.% Ti 50.5(9) wt.% PdO 5.6(2) wt.% TiO_2 ana 2.9(3) wt.%	3.9032(4) 3.8926(2)	59.465(11) 58.984(5)	134 / 0.0072 226 / 0.0043
0.3 mg/cm^2 Pd	Pd 18±1 wt.% Ti 82±1 wt.% НФ[3] TiO_2 ana traces	3.8889(10)	58.81(3)	102 / 0.0095
0.3 mg/cm^2 Pd calcined	Pd 10.4(1) wt.% Ti 60.8(7) wt.% PdO 18.8(3) wt.% TiO_2 ana 9.1(6) wt.%	3.8977(14)	59.21(4)	303 / 0.0032
0.3 mg/cm^2 Pt calcined	Pt 15.3(3) wt.% Ti 75.6(1.1) wt.% TiO_2 ana 9.1(6) wt.%	3.9174(3)	60.115(7)	115 / 0.0085
0.5 mg/cm^2 Pt calcined	Pt 36±1 wt.% Ti 53±2 wt.% TiO_2 ana 11±3 wt.%	3.91608(17)	60.056(4)	155 / 0.0063
0.5 mg/cm^2 Pt	Pt 27.3(4) wt.% Ti 72.7(1.1) wt.% UP[3]	3.9165(2)	60.077(6)	101 / 0.0097
0.7 mg/cm^2 Pd	Pd 35±1 wt.% Ti 65±1 wt.% UP[3]	3.8882(2)	58.782(7)	97 / 0.0099
0.3 mg/cm^2 Pt	Pt 12.1(4) wt.% Ti 87.9(1.5) wt.% UP[3]	3.9198(4)	60.226(11)	99 / 0.0098

Notes: [1] – the quantitative phase ratio refers to the sample's surface; [2] – Ti has a structure type similar to Mg, with a space group of $P6_3/mmc$; [3] – unidentified phase (UP). Broad reflections at 2θ~35.97^0, 40.96^0, and 59.26^0. It may be a titanium hydride (e.g., TiH_2 with a structure similar to CaF_2); [4] – PdO room-temperature modification (pallandite) has a structure type similar to PtS, with a space group of $P4_2/mmc$; [5] – TiO_2 anatase has a space group of $I4_1/amd$.

nanotubes. On the one hand, water serves as a source of oxygen and is necessary for the formation of the oxide film. On the other hand, an increase in water content in ethylene glycol reduces the solution's viscosity and enhances the hydration of fluoride ions, consequently increasing their chemical mobility, which affects the morphology of the formed nanotubes.

The deposition of platinum and palladium on TiO_2 nanotubes results in well-distributed nanoparticles, enhancing the surface's crystallinity and structural arrangement.

The presence of titanium hydride is observed in some samples, possibly indicated by unidentified phases on the XPRD pattern and broad reflections at specific 2θ values.

The primary particle sizes of platinum and

palladium were calculated, showing variations based on the sample and metal load.

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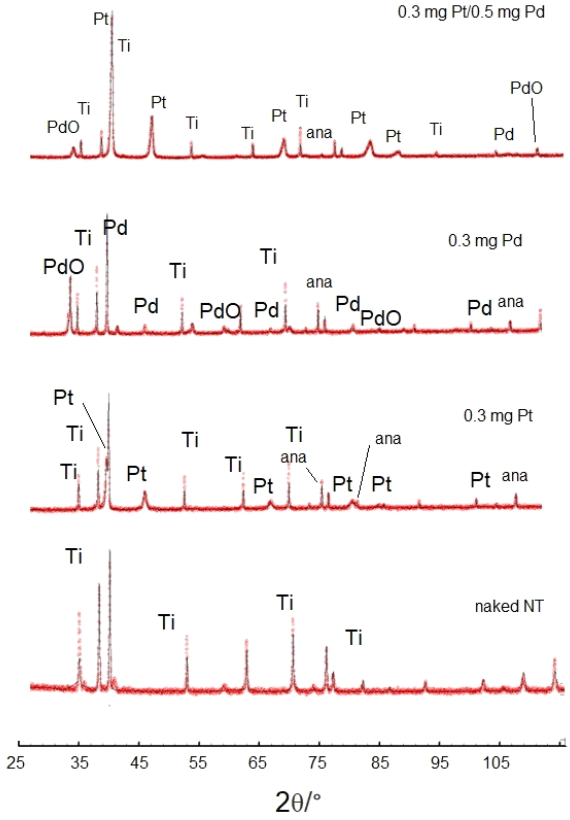

Fig. 2. Observed and calculated X-ray powder profiles for samples coated with 0.3 mg Pt and/or 0.3 mg Pd. Experimental data (circles) and calculated profile (solid line through the circles)

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СТРУКТУРА, МОРФОЛОГІЯ ТА ФАЗОВИЙ СКЛАД ОДЕРЖАНИХ АНОДУВАННЯМ НАНОТРУБОК ДІОКСИДУ ТИТАНУ, ВКРИТИХ ШАРОМ Pt ТА Pd

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Це дослідження присвячене нанотрубкам діоксиду титану (TiO_2) на твердих основах, які можуть знайти

широке застосування як фотокаталізатори та каталізатори. Щоб задовольнити потребу в більш стійких та активних електрокаталізаторах із зниженим вмістом благородних металів, у дослідженні розглядаються субоксиди Ti_nO_{2n-1} як перспективні субстрати для електрокаталізаторів. Привертає увагу той факт, що додавання води до фторовмісного електроліту має вирішальне значення у формуванні морфології нанотрубок TiO_2, що приводить до утворення впорядкованих структур при певних концентраціях води. Також досліджено вплив осадження платини та паладію на структуру і морфологію нанотрубок TiO_2. Електрохімічне нанесення металу підвищує кристалічність поверхні та покращує структуру нанотрубок. У деяких зразках виявлена неідентифікована фаза, можливо, гідрид титану. Отримані дані розкривають потенціал нанотрубок TiO_2 як ефективних електрокаталізаторів, відкриваючи нові можливості для передових застосувань у різних галузях.

Ключові слова: нанотрубки діоксиду титану, морфологія, електроосадження, фазовий склад, мезопориста структура.

STRUCTURE, MORPHOLOGY AND PHASE COMPOSITION OF ANODIZED TITANIUM DIOXIDE NANOTUBES LOADED WITH Pt AND Pd

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