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Tailoring electrochemical efficiency of hydrogen evolution by fine tuning of TiO_x/RuO_x composite cathode architecture

Fedor S. Fedorov,^{1*} Mikhail Y. Vasilkov,^{2,3} Maxim Panov,¹ Dmitry Rupasov,¹ Alexander Rashkovskiy,⁴ Nikolay M. Ushakov,³ Jaeho Lee,⁵ Rolf Hempelmann,^{5,6} Tanja Kallio,⁷ Albert G. Nasibulin^{1,7}

¹Skolkovo Institute of Science and Technology, 3 Nobel St, 121205, Moscow, Russian Federation ²Yuri Gagarin State Technical University, 410054 Saratov, 77 Polytechnicheskaya St, Russian Federation

³Saratov Branch of Kotelnikov Institute of Radioengineering and Electronics of RAS, 410019 Saratov, 38 Zelenaya St, Russian Federation

⁴Systems of Microscopy and Analysis, 121353 Moscow, 100 Novaya St, Russian Federation

⁵Korea Institute of Science and Technology Europe, 1 Campus E7, 66123

Saarbrücken, Germany ⁶Saarland University, 3 Campus Dudweiler Zeile, 66125 Saarbrücken, Germany

⁷Aalto University, Puumiehenkuja, 00076 Aalto, Finland

*Corresponding author:

E-mail: f.fedorov@skoltech.ru

Laboratory of Nanomaterials, Skolkovo Institute of Science and Technology, 3 Nobel Str., 121205, Moscow, Russian Federation

Graphical Abstract

Highlights

- We have fabricated cathode based on TiO_x nanotubes decorated by RuO_x nanowhiskers
- Surface morphology of cathode is tailored to facilitate gas bubble detachment
- A pre-dominant type of hydrogen bubble release is resolved using wavelet analysis
- The best HER efficiency is up to 64% associated with small bubble detachment

Abstract

Here we report an approach to design composite cathode based on TiO_x nanotubes decorated with RuO_x nanowhiskers for efficient hydrogen evolution. We tailor catalytic activity of the cathodes by adjustment of morphology of TiO_x nanotubular support layer along with variation of RuO_x loaded mass and assess its performance using electrochemical methods and wavelet analysis.

The highest energy efficiency of hydrogen evolution is observed in 1 M H_2SO_4 electrolyte to be ca. 64% at -10 mA/cm^2 for cathodes of the most developed area, i.e. smaller diameter of tubes, with enhanced RuO_x loading. The efficiency is favored by detachment of small hydrogen bubbles what is revealed by wavelet analysis and is expressed in pure noise at wavelet spectrum. At increased current density, -50 or -100 mA/cm^2 , better efficiency of composite cathodes is supported by titania nanotubes of larger diameter due to an easier release of large hydrogen bubbles manifested in less periodic events appeared in the frequency region of 5-12 s at the spectra.

We have shown that efficiency of the catalysts is determined by a pre-dominant type of hydrogen bubble release at different operation regimes depending on specific surface and a loaded mass of ruthenia.

Keywords: titania nanotubes; ruthenia; composite cathode; water electrolysis; hydrogen evolution reaction; wavelet analysis

1. Introduction

World's increasing energy consumption accelerates the development and the tailoring of synthesis methods of energy storage chemicals in which the energy is usually preserved in a form of chemical bonds [1]. A major promising energy storage chemical is molecular hydrogen, clean and benign energy source, characterized by large gravimetric storage capacity and simplicity of production just by electrolysis of aqueous solutions [2].

Efficiency of hydrogen generation process is mainly attributed to electrode materials which support low hydrogen evolution (HER) overpotentials. Although, the most efficient catalyst for HER is platinum (Pt) [3,4], it is suggested to be scarce, expensive and to be prone to poisoning by electrolyte impurities, e.g. due to underpotential deposition that leads to decrease in the efficiency over time [5–7]. Recent progress in this field is facilitated by application of non-noble metal materials and composites [8,9]. A method to simultaneously decrease the costs and improve catalyst stability is to employ transition metal oxides and hydroxides, such as Ni/NiO [10,11], some of which still might degrade in acidic environments [12]. Important findings are associated with the use of phosphides (cobalt phosphide, $\text{Fe}_{0.5}\text{Co}_{0.5}\text{P}$, RuP_x @ nitrogen- and phosphorous-codoped carbon nanospheres) both in acidic and in alkaline solutions [13–16], sulfates [17,18] and other materials demonstrating Tafel slope up to 30 mV/dec and good durability. Alternatively, the noble metal materials like ruthenium and ruthenium oxide are stable, both applied for water splitting and rather cost-effective when compared to Pt [19–21]. Ruthenium oxide has been evaluated to efficiently catalyze HER and oxygen evolution reaction (OER) competitively studied along with IrO_2 materials [22–24]. In early works, compact ruthenium oxide layer shows Tafel slope of 40-60 mV/dec in acidic media and high exchange current density $(0.6-5) \cdot 10^{-4} \text{ A/cm}^2$ which is only slightly lower than that for Pt [7,25,26] In alkaline solution RuO_2 layers with

loading 0.5- 2 mg/cm² show Tafel slope in a similar range; in near neutral salt solution HER overvoltage is higher [27]. Edison et al. have shown that Tafel slope of carbon encapsulated RuO₂ nanorodes at stainless steel to be ca. 99.4 mV/dec in 0.5 M H₂SO₄ solution [28].

Catalyst efficiency is also reliant on specific area to be in contact with electrolyte and, thus, is often approached by the use of materials with dimensions at nanoscale [29–32]. Electrocatalytic activity of ruthenia is considered to be influenced by the surface area which may be modified by varying, for instance, the oxide loading, its hydration or the crystallinity [33,34]. The H₂ evolution rate is proportional to the real surface area of the oxide film [27,33] what has facilitated employment of ruthenia-based nanomaterials like nanofibers [35], nanowires [36], nanorods [37– 39], *etc.* Though, the oxide has been shown to be easily blocked by hydrogen bubbles, which screen its surface and deteriorate the performance [19,40,41].

Catalyst morphology should favor bubbles to detach from the surface and mitigate their growth after nucleation not to induce extra stresses in material [42]. This is supported by improvement of electrocatalytic activity for the chlorine evolution reaction in chlor-alkali process when more hydrophilic surface is utilized to promote detachment of hydrophobic gas bubbles when they are still small [43]. It is worth noting that commonly used carbon based supports are hydrophobic and hence, not optimal for bubble detachment, though, when converted to be more hydrophilic might also be oxidized more readily and show weak stability [44,45]. Moreover, the catalyst must be designed to prevent expulsion of electrolyte, e.g. in distributed systems due to a gas adsorption within small pores, which is equivalent to a decrease in real surface area what enhances cathodic potential and is suggested to contribute to the non-linear Tafel behavior [33]. Thus, having a developed surface just at current collector interface without complex porous (distributed) structure becomes more advantageous for long-term performance.

These requirements can be achieved by a precise control of surface morphology at nanoscale, e.g., using substrates made of titania nanotubes (NTs), those dimensions can be easily tuned [46–49] whereas incorporation of active material into Ti or TiO_2 is acknowledged to facilitate electrocatalytic activity, extend lifetime and enhances stability of ruthenia [50–52]. Recent report has already found titania nanotube to serve as a platform for ruthenia and iridium dioxide catalysts for OER reaction exhibiting an onset potential of 0.84 V vs. standard hydrogen electrode with faradaic efficiency of 99% at 2 V [53]. Therefore, modification of nanotubes by microquantity of RuO_2 nanoparticles using its precursor should beneficially support confinement of ruthenia at TiO_2 nanotube walls and in voids up to TiO_2/Ti interface what allows to create a composite with developed area immobilized on a current- collector surface [54]. However, the evaluation of efficiency depending on specific surface and loading of active material remains a challenging task and requires systematic studies including analysis of characteristics of gas bubble detachment.

Here, we synthesize a novel composite cathode material, TiO_x nanotubes decorated with RuO_x nanowhiskers, emphasizing precise tailoring of its surface morphology to favor gas bubble detachment for improved HER performance. For the first time, we have tested wavelet analysis for assessment of features of hydrogen bubble growth and detachment in order to evaluate its influence on overall catalyst activity.

2. Experimental

2.1 Formation of TiO_x nanotubes

Titania NTs were prepared by electrochemical anodization of Ti at constant voltage according to known protocols [55]. Prior to anodization surface of Ti commercial discs (>99.5% Ti, Alfa Aesar, Germany), 15 mm diameter, were mechanically wet- polished with SiC paper (stepwise applied from grid 200 and up to the grid 4000) at 400-500 min⁻¹ using Struers DAP-U (Struers Ins., Denmark) grinder. Then, the disk surface was chemically etched at room temperature for 5-10 seconds to obtain a mirror polish. The composition of etching solution is shown in Table S1 [56]. To be further anodized the polished samples were pressed in custom-made holder where they were electrically connected via a gold spring and vertically positioned at 5-10 mm distance from a glassy carbon electrode disc which was utilized as a cathode.

The anodization was conducted at constant voltage 10, 20 or 30 V for 60 min at room temperature for 1 hour using power source Keithley 2410 (Keithley Instruments Inc., USA) from electrolyte consisted of glycerol (Sigma-Aldrich, ≥99.5%) and deionized water (18.2 MΩ·cm) in mass ratio 3:1 with addition of 0.7-0.8 wt-% ammonium fluoride NH₄F (Sigma-Aldrich, 98.0%).

After preparation, TiO_x NTs@Ti were cleaned in ethanol, deionized water and annealed in automated vacuum oven PEO-601 (ATV Technologie GmbH, Germany) in air at 450 °C for 150 min to stabilize the titania in anatase phase (see also Supporting information) [54]. Basic geometric parameters of obtained NTs are listed in Table 1 what suggest that increase of the voltage yields increase of inner diameter, wall thickness of NTs while their density decreases. The height of nanotubular layer was ca. 1 μm [54].

Table 1. Basic geometric parameters of obtained TiO_x NTs

Anodic voltage, V	Average inner diameter, nm	Average wall thickness value, nm	Tubes number per unit area, cm ⁻²
10	34.4±0.7	9.2±0.4	26.0·10 ⁹
20	68.9±1.2	11.2±0.4	6.6·10 ⁹
30	108.3±3.4	12.8±0.7	4.0·10 ⁹

2.2 Modification of TiO_x nanotubes with RuO_x

To prepare a composite cathode we immersed TiO_x NTs@Ti in 0.030 M RuCl₃ solution for 15 min, which was prepared by dissolution RuCl₃·xH₂O (Alfa Aesar, 38% Ru, Johnson Matthey Comp., USA) in deionized water. Afterwards, samples' surface was dried in air and subjected to heat treatment in an oven in air atmosphere at 650 °C for 20 min to form ruthenia [57,58]. The oxidation can be described by the following reaction:

The applied temperature settings were found in preliminary experiments not to induce extra stresses due to volume expansion caused by oxide formation (not presented here). At a final stage the samples were cooled down to room temperature, cleaned in deionized water and dried in air. We varied a number of cycles of RuO_x synthesis from 1 up to 5.

2.3 Material characterization

Oxidation of ruthenium chloride was first tested by simultaneous thermal analysis (STA), which was a combination of differential temperature analysis (DTA) with thermogravimetric capabilities (TGA) coupled with the mass-spectrometer at NETZSCH STA 449 F3 Jupiter® unit. We transferred RuCl₃ solution in Al₂O₃ crucibles and let it dry in a desiccator at 60 °C for 3-4 h. The samples were studied in range starting from room temperature to 650 °C with 20 min isothermal segment at the 650 °C in synthetic air. Heating rate was set to be 50 °C/min. This experiment simulated optimum conditions of ruthenia/titania cathode preparation. To further examine stabilization of ruthenia phase we carried our STA measurements up to 1100 °C at the rate of 10 °C/min whose results we presented in [Supporting information](#).

We characterized surface morphology of RuO_x/TiO_x NTs by scanning electron microscopy (SEM) using FEI Quanta 200 (FEI Comp., USA). During the SEM observations we tilted RuO_x-modified samples to 40° to better evaluate its morphology. Studies of the obtained ruthenia were conducted using transmission electron microscopy (TEM), FEI Tecnai G2F20 S-Twin TMP (Eindhoven, The Netherlands), under accelerating voltage of 200 kV. The same unit was applied for electron diffraction to analyze crystal structure of obtained ruthenia and titania (NTs separated from Ti substrate) [54]. We applied fast Fourier transform (FFT) and

@SingeCrystal 3 software for identification of phase and preferential direction of growth.

Material's chemical composition studies were carried out by X-ray photoelectron spectroscopy (XPS) using electron spectrometer PHI VersaProbe II 5000 microprobe spectrometer (Al K α source, 1486.7 eV) with spot a diameter of 100 μ m, analyzer pass energy equal 93.90 eV (survey spectrum) and 23.5 eV (other spectra).

The survey spectrum and Ru3d, O1s and Ti2p core levels spectra were recorded and then refined by several scanning. We used @CasaXPS software package for deconvolution of multicomponent spectra; peaks were approximated by a Lorentz- Gauss function.

2.4 Electrocatalytic measurements and noise analysis

Electrochemical measurements were performed using BioLogic SP-150 (Bio-Logic Sci. Ins., France) potentiostat-galvanostat or Novocontrol alpha A.N. system (Novocontrol Technologies GmbH & Co. KG, Germany). The measurements were carried out in custom-made three-electrode cell with TiO_x nanotubes modified by RuO_x serving as a working electrode, graphite rod as a counter electrode and Ag/AgCl_{sat.} as a reference electrode. All potentials are recalculated and are quoted *versus* reversible hydrogen electrode (RHE), $E(vs\ RHE) = E(vs\ Ag/AgCl_{sat.}) + E_0(Ag/AgCl_{sat.}) + 0.0592 \cdot pH$, where $(E_0(Ag/AgCl_{sat.}) = 0.197\ V$ [8]. We avoided to use N₂ purging and use of *iR* compensation since real applications are not to include it, though, are focused on efficiency gain. Cyclic voltammetry was recorded for all samples with the scan rate 25 mV/s in range from 50 mV to -700 mV in 1 M H₂SO₄. (Cyclic voltammetry studies were also performed in 0.1 M NaOH and 0.1 M Na₂SO₄ electrolytes). Galvanostatic experiments were conducted in two-electrode configuration at current densities of -10, -50 and -100 mA/cm². Hydrogen generation time was set to be 10 min; the evolving gas was collected using a reverted micro- burette method. We performed at least five parallel measurements at room temperature to investigate reproducibility of the results. Durability test was performed at -10 mA/cm² for 100 h.

Calculations of energy consumption E (kJ/mol) for generation of 1 mol H₂ were carried out according to the equation:

$$E = \frac{\int U dt \cdot I}{n(\text{H}_2)}, \quad (2)$$

where U is the cell voltage (V), t denotes a time (s), I is a current applied to electrodes (A), $n(\text{H}_2)$ is an amount of collected hydrogen (mol), calculated from the volume of generated H_2 and corrected to normal conditions [59].

The energy efficiency η (%) for hydrogen evolution:

$$\eta = \frac{283.3}{E} \cdot 100\%, \quad (3)$$

where 283.3 kJ/mol is standard molar formation enthalpy of liquid water, E is energy consumption, kJ/mol.

The potential noise was analyzed by means of wavelet analysis. The continuous wavelet transform of the potential noise was performed by *gaus4* wavelet (the fourth derivative of Gaussian function) [60] using @Matlab software.

3. Results and discussion

3.1 Structure and composition of $\text{RuO}_x/\text{TiO}_x$ NTs composite cathode

Prior to fabrication of the composite, we have analyzed thermal behavior of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$. To evaluate the material changes induced by the treatment we have simulated optimum treatment conditions by STA whose results are presented in Figure 1a. Thermogravimetry is characterized by two main regions which are manifested by pronounced mass change. The first one is due to water removal, starting at about 90 °C. The second region corresponds well

to oxidative decomposition of RuCl_3 with onset at 370 °C. These results are supported by mass-spectrometric ion intensity data which show water ($M/Z = 18$) and chlorine ($M/Z = 35$), appearance in the studied temperature interval due to the oxidative decomposition of the material. Ion current suggests that water is being removed in the temperature interval starting from 80 °C up to 400°C. Chlorine liberation is observed at 350 °C and is being almost finished when the temperature reaches 650 °C. Presence of few peaks hints on occurring overlapping reactions of its liberation [58]. The DSC curve follows the TGA curve and corresponds to the observed changes. The mass is retained at ca. 57% when temperature reaches 650 °C what corroborates well with appearance of RuO_2 .

Increase of annealing temperature does not yield major mass changes. When heated up to 1100 °C with 10 °C/min, the mass is stabilized at about 57% already at temperature of 450 °C steadily decreasing to about 54% at 880 °C (See [Supporting information](#)). These results support that a prominent change to be reached even by the rather quick heating. An observed mass loss corresponds well to ruthenia when oxidation of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ to RuO_2 is considered.

Ruthenia, which is obtained by the thermal treatment of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ in STA experiment, has been subjected to TEM studies. TEM observations conducted just after the treatment show true nanoparticles and nanowhiskers of ruthenia (Figure 1b,c). The whiskers prevail and are characterized by length of ca. 100 – 150 nm with the width of ca. 10-30 nm. The whiskers are crystallized in tetragonal phase, space group $P 4_2/m n m$ with cell parameters equal $a = 4.4931 \text{ \AA}$, $c = 3.1064 \text{ \AA}$ and are preferentially oriented in [] direction as supported by FFT analysis of the HR-TEM image (Figure 1c, inset) [61]. Increasing of annealing temperature results in the increase of the particle size (in the synthetic air atmosphere, see [Supporting information](#)).

Figure 1. Characterization of RuO_x formation and its structure. STA and mass spectrometry results of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ annealing in synthetic air at 50 $^{\circ}\text{C}/\text{min}$ to 650 $^{\circ}\text{C}$ (a). TEM overview of RuO_x nanowhiskers (b) and a single whisker (c), inset: FFT analysis results of a single whisker. Color online.

Pristine titania NTs obtained at 20 V are presented in Figure 2a and suggest NTs to be highly-ordered and densely-packed forming quite homogeneous layer. However, there are voids between the tubes what have been already shown in [54]. Modification of TiO_x NTs using $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ leads to formation of an oxide RuO_x film at its surface what is accompanied by appearance of the oxide at the tubes surface and in the intertube space (filling of voids) (Figure 2b,c). Though, oxide formation does not influence the layer structural integrity (as the thermal treatment parameters have been optimized in pre-experiments). Insets in the Figure 2a and in the Figure 2b show the appearance of samples before and after modification by RuO_x .

Figure 2. Morphology and chemical composition of the obtained cathode material, 20 V TiO_x NTs modified by RuO_x , 5 cycles: SEM images of TiO_x NTs (a) and $\text{RuO}_x/\text{TiO}_x$ NTs (b,c) samples. XPS core level spectra of Ru (d), O (e) and Ti (f). (* in Figure 2d is for “unscreened final state”). Color online.

Chemical composition of the obtained composites has been examined by XPS whose data have enabled us to evaluate peaks related to Ru, O, Ti and C elements presented on the sample's surface. Survey spectrum is given in [Supporting information](#) file. Figure 2d demonstrates the fitting results of Ru3d-C1s region of binding energies. We have decided not to clean the surface from adventitious carbon and to apply curve fitting procedure to extract to Ru3d peak features from overlapping region with carbon C1s. Since Ar^+ ions sputtering of d-metals oxides leads to partial reduction of the metal due to higher removal ratio of oxygen. Due to specific electronic structure Ruthenium oxides have strong unscreened final states

near the main asymmetric components of Ru3d peak at 282.4 (Ru 3d_{5/2}) and 286.6 (Ru 3d_{3/2}) eV [62–64]. The oxide peaks are at 280.6 and 284.8 eV correspondingly for RuO₂ 3d_{5/2} and RuO₂ 3d_{3/2}. Adventitious carbon has been split into three states (284.8 eV for C-C bonds; 286.1 eV for C-O bonds; 289.3 eV for C=O bonds) to get the best fitted model (red curve) of the spectra. O1s core level spectrum deconvolution (Figure 2e) indicates Ru-O and Ti-O bonds with O 1s peak at 529.4 and 530.05 eV, correspondingly [65,66]. Peak at 531.3 eV supports the presence of C-O groups due to contamination of the surface. Ti 2p_{3/2} is positioned at 458.9 eV hinting on TiO₂ and is known to overlap with Ru 2p_{3/2} at 461.9 and 484.15 eV (Figure 2f). Other peaks and satellites are referred to Ti: Ti-loss (1) at 472.45 eV, Ti- loss (2) at 477.6 eV and Ti 2p_{1/2} at 464.6 eV.

Based on the relative intensity of the Ru 3d_{5/2}, Ti 2p_{3/2} and O 1s peaks we have estimated atomic ratio of elements in a TiO_x NTs matrix layer depending on tubes diameter (voltage) and number of modification cycles. These results are summarized in Table 2. XPS analysis of these samples has showed that the maximum Ru concentration is obtained after five cycles of modification of sample with nanotubular layer obtained at 20 V. The range of concentrations varies from 1.1 to

3.5 at.%. Increasing the number of cycles from 1 to 5 favors some increase in the Ru concentration from about 2.7 to 3.5 at.%. The less Ru content has been found in the sample prepared at 30 V. An origin of a greater signal from titania in the latter case might be greater tubes' diameter what favors most of the signal to stem from the tubes' mouth. Therefore, we expect to realize ruthenia nanostructures confinement within titania nanotubes and voids.

Table 2. Atomic concentration of O, Ti, Ru calculated from XPS data. The number of applied RuO_x deposition cycles is given in brackets after the applied voltage.

	10 V (5)	20 V (1)	20 V (3)	20 V (5)	30 V (5)	Reference
O, at. %	67.4	69.6	61.7	60.1	67.4	66.1
Ti, at. %	30.5	27.7	35.0	36.4	31.5	33.9
Ru, at. %	2.1	2.7	3.4	3.5	1.1	-

3.2 Electrocatalytic properties of RuO_x/TiO_x NTs

Electrochemical performance has been assessed by recording cyclic voltammetry curve (Figure 3a,b) at a scan rate 25 mV/s. In case of pristine tubes, HER is characterized by high overpotential with onset value close to -540 mV. RuO_x introduction changes HER onset potential drastically to be equal ca. -230 mV at -0.5 mA/cm² for samples obtained with 5 cycles of ruthenia deposition. Moreover, there is a significant increase in current density when compared the pristine tubes which are prepared at anodization voltage of 20 V. Increase of RuO_x content is also manifested in increase of current density. The subsequent modification by 3 and 5 cycles demonstrates current density improvement up to 3 times (at -500 mV) when compared to a single cycle of modification by RuO_x. Tube diameter variation (samples obtained at 10, 20 and 30 V and modified by 5 cycles of RuO_x deposition) does not show significant improvement in the catalytic performance of these samples (Figure 3b) which should be due to a full coverage of the samples' surface. We have calculated a Tafel slope to be about 131, 123 and 110 mV/dec at potentials of ca. -230 mV for samples which are prepared with nanotubes made at 10, 20 and 30 V and using 5 cycles of ruthenia deposition respectively (considering low *iR* drop in 1 M H₂SO₄ electrolyte). The obtained values might suggest Volmer-Heyrovsky pathway of HER [44]; the slope values are in good agreement with the data obtained by Edison et al. for carbon encapsulated RuO₂ nanorodes at stainless steel in 0.5 M

H₂SO₄ solution [28]. For the cathodes with smaller loading of ruthenia Tafel slope appears to be higher. We have also tested the cathodes in 0.1 NaOH and in 0.1 Na₂SO₄ electrolytes, however, their activity is less expressed, probably due to lower concentration of hydronium ions (these results are presented in [Supporting information](#) file).

Figure 3. Characterization of catalytic activity of obtained composites. Cyclic voltammetry curves recorded in 1 M H₂SO₄ at scan rate 25 mV/s for TiO_x NTs modified by different number of deposition cycles of RuO_x (a) and TiO_x NTs obtained at different anodizing voltage modified by 5 deposition cycles of RuO_x (b) compared with the TiO_x NTs obtained at 20 V. Cell voltage recorded in galvanostatic mode at -10 (c), -50 (d), -100 mA/cm² (e) in 1 M H₂SO₄ for TiO_x NTs obtained at different anodizing voltage and modified by different number of cycles of RuO_x deposition and corresponding energy efficiency of hydrogen generation (f, g, h). Color online.

Tests of efficiency of hydrogen generation have been performed in a galvanostatic mode at -10, -50 and -100 mA/cm² for 10 min. We have collected hydrogen in order to measure its volume and have recorded cell voltage to evaluate the process efficiency. Cell voltage changes agree well with the applied current density change and a number of RuO_x deposition cycles: increase of current density yields increase of the cell voltage; increase of amount of cycles favors decrease of the cell voltage (Figure 3c,d,e). The cell voltage values remain to be quite stationary over the recorded time period.

Energy efficiency of HER at different current densities calculated according to eq.

(3) is depicted in Figure 3f,g,h depending on tube inner diameter and number of RuO_x deposition cycles. For the same number of cycles, the efficiency is reduced with increase of current density. Oppositely, increase in the number of cycles of ruthenisation which is shown for the samples with tubes obtained at 20 V facilitates the HER whose efficiency correspondingly changes from about 58 to 63% at -10 mA/cm² for 1 to 5 cycles. Similar trends are observed at greater current densities. The efficiency of HER on unmodified TiO_x NTs is about 36%.

Moreover, at current density -10 mA/cm² the sample obtained at 10 V with 5 cycle of RuO_x deposition shows the maximum efficiency of ca. 64% while the samples obtained at 30 V (with 5 cycles of RuO_x deposition) is characterized by lower efficiency of 56% when compared the other samples with the same amount of cycles at this current density. This is due to decrease of surface area and, probably, better attachment of hydrogen bubbles inside the tube interspace (which is greater pronounced in the case of sample prepared at 30 V). However, at higher current densities cathodes with tubes of greater diameter show better energy efficiency which is expressed in change from 46% to 49% correspondingly for cathodes with tubes obtained at 10 V and at 30 V (5 cycles of RuO_x deposition) tested at 100 mA/cm² and about 50% for the 20 V sample.

Thus, the most efficient release of hydrogen at -100 mA/cm² occurred on the cathode with tubes of greater diameter, 68.9±1.2 and 108.3±3.4 nm, which are modified with 5 cycles of deposition of RuO_x whereas the most efficient release at -10 mA/cm² is observed for sample with minimal diameter, 34.4±0.7 nm, i.e. greater specific surface. To investigate material

durability, we have tested the most efficient cathode at current density -10 mA/cm^2 for 100 hours. The test results are depicted in the Figure 4. After 10 hours of electrolytic cell operation, the recorded potential increases to ca. -400 mV and then is stabilized at -150 mV after 50 hours what suggests some improvement of performance during the test. The morphology of the cathode surface after durability test is represented by nanotubular TiO_x layer which is decorated by agglomerated particles (Figure 4, inset). The observed agglomeration might be associated with the improvement of activity.

Figure 4. Chronopotentiometric durability test of cathode material, 20 V TiO_x NTs modified by RuO_x , 5 cycles, performed in 1 M H_2SO_4 for 100 h at current density -10 mA/cm^2 . Inset: SEM image of the cathode after the test.

3.3 Noise analysis

To further evaluate the obtained data, we have applied wavelet analysis to recorded potential transients. The wavelet power spectrum (WPS) visualizes the periodic components of 1-12 s (see Figure 5). The chosen range of periods is determined by the overall length of the time series (100 s) and the cone of influence of the wavelet transform (solid black line in the Figure 5). In the case of 20 V TiO_x NTs modified with RuO_x , 1 cycle, at -10 mA/cm^2 we could observe the pure noise of lower power in the spectrum which corresponds to the detachment of small bubbles (Figure 5a-c). Under increased current density, especially in the case of -50 or -100 mA/cm^2 , we see certain periodic events whose periods are in the region

of 4-8 s for - 50 mA/cm² and greater than 8 s for -100 mA/cm². Significant increase in the magnitude of wavelet spectra is facilitated by the yield of current density. Increase of period corroborates well and marks the increase in the size of bubbles due to gas adsorption which should be also accompanied by their coalescence. Thus, less efficient samples are characterized by periodic events with periods of 8-12 s what should be due to detachment of bubbles those size is reasonably large. This might hint on the fact that bubbles do not detach after nucleation, though, continue their growth adsorbing gas from the surface and the solution supported by increased growth speed at greater rate of hydrogen generation.

Figure 5. Time recording of the potential fluctuations induced by HER in three- electrode configuration in 1 M H_2SO_4 at different current density on TiO_x NTs obtained at 10, 20 and 30 V anodizing voltage and modified by different number of cycles of RuO_x deposition and its corresponding wavelet power spectrum: 20 V, 1 cycle RuO_x at (a) -10 mA/cm^2 , (b) -50 mA/cm^2 , (c) -100 mA/cm^2 ; $\text{TiO}_x/\text{RuO}_x$ cathodes measured at 100 mA/cm^2 (d) 20 V, 3 cycles, (e) 20 V, 5 cycles, (f) 10 V, 5 cycles, (g) 30 V, 5 cycles. The black lines represent the cone of influence of wavelet transform, i.e. the region, where the wavelet transform is affected by edge effects. Color online.

Thus, these results suggest that tuning of morphology might favor a specific mode (regime) of bubble growth or detachment matching the particular current density.

A series with different number of RuO_x deposition cycles are characterized, first, by decrease an amplitude of the spikes, and, second, show a decrease of big jumps of lower frequency for the TiO_x NTs obtained at 20 V as number of cycles grows (Figure 5c,d,e) what explicitly manifested at -100 mA/cm². These data correlates well with the calculated efficiency of HER for these samples.

Moreover, an increase of the current density reverts the efficiency trend. The efficiency improves at -50 and at - 100 mA/cm² for composites based on TiO_x NTs with a greater diameter (see Figure 5f,e,g). Although, periodic events of low frequency are observed and remain for all samples, in case of greater tubes' diameter their magnitude is decreased. These results coincide well with a change of electrolysis regime for cathode composite RuO_x/TiO_x when at low current densities amount of catalytically active sites plays a major role and kinetic control dominates whereas at high current densities mass transfer should prevail.

4. Conclusions

We have demonstrated the approach to fabricate composite cathode based on TiO_x nanotubes decorated with RuO_x nanowhiskers with high efficiency towards HER. The efficiency improves by increasing the amount of loaded RuO_x and for the most developed area is ca. 64%, when the current density of -10 mA/cm² is applied. This is favored by easier detachment of small bubbles without significant growth and coalescence. At higher current densities we have observed appearance of periodic events in the region of 5-12 s what stem from detachment of large hydrogen bubbles after their growth and coalescence. In these conditions, composite cathodes based on the tubes with greater diameter demonstrate better efficiency due to an easier release of large hydrogen bubbles (after their growth and coalescence) with less periodic events observed in this frequency region.

Thus, using wavelet analysis, we have managed to resolve a type of pre-dominant hydrogen bubble release which, as we have shown, determines efficiency of the catalysts at different

operation/kinetic regimes depending on specific surface and a loaded mass of ruthenia.

The authors declare no competing financial interest.

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Supporting Information

to paper entitled

**Tailoring electrochemical efficiency of hydrogen evolution by fine tuning of TiO_x/RuO_x
composite cathode architecture**

by

Fedor S. Fedorov,^{1*} Mikhail Y. Vasilkov,^{2,3} Maxim Panov,¹ Dmitry Rupasov,¹ Alexander
Rashkovskiy,⁴ Nikolay M. Ushakov,³ Jaeho Lee,⁵ Rolf Hempelmann,^{5,6} Tanja Kallio,⁷ Albert G.
Nasibulin^{1,7}

¹Skolkovo Institute of Science and Technology, 3 Nobel St, 121205, Moscow, Russian Federation

²Yuri Gagarin State Technical University, 410054 Saratov, 77 Polytechnicheskaya St, Russian Federation

³Saratov Branch of Kotelnikov Institute of Radioengineering and Electronics of RAS, 410019 Saratov, 38
Zelenaya St, Russian Federation

⁴Systems of Microscopy and Analysis, 121353 Moscow, 100 Novaya St, Russian Federation

⁵Korea Institute of Science and Technology Europe, 1 Campus E7, 66123 Saarbrücken, Germany

⁶Saarland University, 3 Campus Dudweiler Zeile, 66125 Saarbrücken, Germany

⁷Aalto University, Puumiehenkuja, 00076 Aalto, Finland

*Corresponding author:

E-mail: f.fedorov@skoltech.ru

Laboratory of Nanomaterials, Skolkovo Institute of Science and Technology,
3 Nobel Str., 121205, Moscow, Russian Federation

Composition of etching solution applied for Ti polishing

Composition of etching solution for Ti polishing is presented in [Table S1](#).

[Table S1](#). Composition of etching solution.

Chemicals	Concentration, wt.-%	Contents in etching solution, wt.-%
Nitric acid HNO ₃ (reagent, Merck, Germany)	65	30
Hydrofluoric acid HF (technical, Sigma-Aldrich, USA)	40-45	28
Sulfuric acid H ₂ SO ₄ (ACS, Emsure, Germany)	98	40
Acetic acid CH ₃ COOH (reagent, VWR Chemicals, Germany)	100	2

SAED of titania nanotubes before and after annealing at 450 °C

The NTs are crystallized in anatase phase with d-values equal 1.41, 1.66, 1.89, 2.48 and 3.46 Å what corresponds to [220], [211], [200], [103] and [101] crystal planes (ICSD 9852).

Figure S1. Selected area electron diffraction for TiO_x NTs before (a) and after (b) annealing at 450 °C.

Simultaneous Thermal Analysis

Increase of annealing temperature does not yield major mass changes. When heated with 10 °C/min, the mass is stabilized at about 57% already at temperature 450 °C steadily decreasing to about 54% at 880 °C. The results suggest major mass changes to start at about 100 °C and 350 °C.

Figure S2. Thermogravimetry results of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ annealing in synthetic air at 10 °C/min to 1100 °C

TEM studies of RuO_x obtained at optimized conditions

TEM and SAED results for RuO_x obtained by heating to 650 °C with a rate of 50 °C/min annealing for 20 min.

Figure S3. Survey view of RuO_x particles obtained by annealing at 650 °C for 20 min with SAED ring pattern.

TEM studies of RuO_x heated to 1100 °C

Annealing to 1100 °C facilitates formation of cubic-like particles whose dimensions vary from 200 nm to 1.5 μm . FFT and SAED patterns suggest it to be the same phase as in the case of annealing at 650 °C, precisely, tetragonal phase, space group $P 4_2/m n m$ with cell parameters equal $a = 4.4931 \text{ \AA}$, $c = 3.1064 \text{ \AA}$.

Figure S4. Survey view of RuO_x particles obtained by annealing to 1100 °C, 10 °C/min, HR-TEM image and corresponding FFT pattern and SAED results.

XPS data

The analysis of survey XPS spectra show presence of C, O, Ti and Ru elements. It also shows that RuO_x film presents on the surface of all investigated samples. It is important to note, that practically all intensive lines of Ru overlap with other core-level lines. Ru4p core-level is close to Ti3s , and Ru3p3 overlaps with Ti2p doublet. Moreover, Ru3d doublet surrounds C1s peak that appears from adventitious carbon. So, to perform quantitative analysis of elements concentrations for RuO_x on TiO_x it is necessary to perform detailed decomposition by curve fitting procedure for three regions at binding energies corresponding to the following particular spectra: O1s (near 530 eV), C1s-Ru3d (near 284 eV) and Ti2p-Ru3p (near 465 eV).

Figure S5. Survey XPS spectra for TiO_x NTs obtained at 20 V anodizing voltage and TiO_x NTs obtained at 10, 20 and 30 V modified by different number of cycles of RuO_x deposition (1-5).

Figure S6. Ru3d and C1s XPS spectra obtained from a - TiO_x (20 V), b- RuO_x (5 cycles) /TiO_x (10 V); c- RuO_x (1 cycle) /TiO_x (20 V); d- RuO_x (3 cycles) /TiO_x (20 V); e- RuO_x (5 cycles) /TiO_x (20 V); f- RuO_x (5 cycles) /TiO_x (30 V).

Figure S7. O1s XPS spectra a - TiO_x (20 V), b- RuO_x (5 cycles) /TiO_x (10 V); c- RuO_x (1 cycle) /TiO_x (20 V); d- RuO_x (3 cycles) /TiO_x (20 V); e- RuO_x (5 cycles) /TiO_x (20 V); f- RuO_x (5 cycles) /TiO_x (30 V).

Figure S8. Ti2p-Ru3p XPS spectra a - TiO_x (20 V), b- RuO_x (5 cycles) /TiO_x (10 V); c- RuO_x (1 cycle) /TiO_x (20 V); d- RuO_x (3 cycles) /TiO_x (20 V); e- RuO_x (5 cycles) /TiO_x (20 V); f- RuO_x (5 cycles) /TiO_x (30 V).

Electrochemical performance in alkaline and near-neutral electrolytes

We have studied the performance of the cathodes in 0.1 M Na₂SO₄ and in 0.1 M NaOH to check an influence of electrolyte pH.

Figure S8. Cyclic voltammetry curves: recorded at scan rate 25 mV/s for TiO_x NTs modified by different number of deposition cycles of RuO_x and TiO_x NTs obtained at different anodizing voltage modified by 5 deposition cycles of RuO_x compared with the TiO_x NTs obtained at 20 V in 0.1 M Na₂SO₄ (a,b) and in 0.1 NaOH (c,d).

The curves obtained in near-neutral electrolyte show onset potential of hydrogen evolution reaction to change from -430 to 480 mV at -0.5 mA/cm² for most of the samples. For the cathode which is based on titania nanotubes anodized at 20 V with 1 cycle of RuO_x deposition the onset potential equals -745 mV what is comparable with the onset potential of the cathode based on pristine TiO_x nanotubes (-770 mV). Calculated Tafel slope is rather great in this case exceeding 200 mV/dec.

The onset potential in alkaline electrolytes varies from -265 to -15 mV at -0.5 mA/cm^2 which is much greater comparing with cathodes without deposited ruthenia (- 413 mV). Still, the calculated Tafel slope is in the range from 170 to 250 mV/dec.

Results of wavelet analysis

Time recording of the potential fluctuations induced by HER in three-electrode configuration in 1 M H_2SO_4 at different current density on TiO_x NTs obtained at 10, 20 and 30 V anodizing voltage and modified by different number of cycles of RuO_x deposition and its corresponding wavelet power spectrum.

Figure S10. Potential transient and corresponding wavelet power spectra for TiO_x NTs obtained at 20 V, 1 cycle RuO_x at -10 mA/cm², -50 mA/cm², and -100 mA/cm². The black lines represent the cone of influence of wavelet transform, i.e. the region, where the wavelet transform is affected by edge effects.

Figure S11. Potential transient and corresponding wavelet power spectra for TiO_x NTs obtained at 20 V, 3 cycles RuO_x at -10 mA/cm², -50 mA/cm², and -100 mA/cm². The black lines represent the cone of influence of wavelet transform, i.e. the region, where the wavelet transform is affected by edge effects.

Figure S12. Potential transient and corresponding wavelet power spectra for TiO_x NTs obtained at 20 V, 5 cycles RuO_x at -10 mA/cm², -50 mA/cm², and -100 mA/cm². The black lines represent the cone of influence of wavelet transform, i.e. the region, where the wavelet transform is affected by edge effects.

Figure S13. Potential transient and corresponding wavelet power spectra for TiO_x NTs obtained at 10 V, 5 cycles RuO_x at -10 mA/cm², -50 mA/cm², and -100 mA/cm². The black lines represent the cone of influence of wavelet transform, i.e. the region, where the wavelet transform is affected by edge effects.

Figure S14. Potential transient and corresponding wavelet power spectra for TiO_x NTs obtained at 30 V, 5 cycles RuO_x at -10 mA/cm², -50 mA/cm², and -100 mA/cm². The black lines represent the cone of influence of wavelet transform, i.e. the region, where the wavelet transform is affected by edge effects.