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## Hydrothermal synthesis and characterization of nanostructured titanium monoxide films

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At the present time, the formation of titanium monoxide ( $TiO_x$ ) two dimensional (2D) species with distinct composition, size, shape, and a significantly reduced bandgap ( $E_g$ ) value compared to  $TiO_2$  is of great scientific and practical importance. This paper describes our findings investigating Ti surface oxidation for the formation of  $TiO_x$  films possessing a densely-packed nanoplatelet morphology and a low bandgap value. This goal was herein achieved by the hydrothermal treatment of the Ti surface in selenious acid solution kept at a slightly alkaline pH. Furthermore, the nanoplatelet design not typical for  $TiO_2$  porous films was created by this method for the first time. The formation of titanium monoxide, particularly  $TiO_{0.84}$ , as a major crystalline phase, was verified by XRD and confirmed by EPR investigations. It is worth noting that these nanoplatelet-shaped films with a thickness of 0.1–0.25  $\mu m$  exhibited a very large shift of their light absorption threshold, down to 1.29 eV, compared to the  $E_g$  of anatase  $TiO_2$  and a surprising 70% porosity determined via simulation of experimental reflection plots. It is anticipated that this unique  $TiO_x$  nanomaterial will pave the way for new investigations and applications.

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### Introduction

Titanium dioxide,  $TiO_2$ , belongs to the group of materials that were most intensely investigated during the past three decades due to their unique optical, dielectric, catalytic properties, chemical resistance, mechanical hardness, nontoxicity and simple processing at a low cost. The crystalline forms of  $TiO_2$ -anatase,  $TiO_2$ -rutile and  $TiO_2$ -brookite polymorphs are well documented. Nanostructured anatase and rutile crystallites possess excellent optical absorption performance under UV light illumination due to their bandgap values of 3.2 eV and 3.06 eV, respectively. They are successfully used in the modern photocatalysis, solar cell devices,<sup>1–3</sup> gas sensors,<sup>4,5</sup> and protective and multilayered coatings.<sup>6</sup> To tune the absorption edge of  $TiO_2$  in the visible light region, the doping of titania with various elements both in the Ti and O sublattice positions has been proposed and discussed in numerous papers.<sup>7–13</sup> Besides, the hybridization of titania with lower bandgap semiconductor nanoparticles and quantum dots, such as  $Cu_2O$ ,<sup>14</sup>  $CuSe_x$ ,<sup>15</sup>  $CdSe$ ,<sup>16</sup> etc. has been proposed.

Nonstoichiometric semiconducting titanium oxides, namely titanium suboxides, containing structural vacancies in both titanium and oxygen sublattices with a general formula  $Ti_nO_{2n-1}$ , where  $n \geq 2$ , represent a group of less known low band gap materials, well reviewed in the recent years by the Chen<sup>17</sup>

and Xu<sup>18</sup> groups. The experimental results have shown that the  $n$  value usually varies between 3 and 10,<sup>6</sup> although significantly higher  $n$  values were also reported.<sup>19–21</sup> The excellent electric conductivity, and visible light absorption are also characteristic features of titanium monoxides,  $TiO_x$  ( $x < 2$ ), making them very suitable for prospective applications in electronic and optoelectronic devices, photo catalysis, batteries, etc. For example, the presence of vacancies in  $TiO_{1.0}$  results in an  $E_g \approx 2.0$  eV, as reported by Gusev.<sup>22</sup> To date different precursors and synthesis methods have been reported for  $Ti_nO_{2n-1}$  and  $TiO_x$  fabrication.<sup>23–28</sup> From these reports, titanium monoxides can be synthesized from raw  $TiO_2$  powders by high temperature reduction with hydrogen,<sup>23,24</sup> carbon<sup>25,26</sup> and active metals such as Ti, Na, Ca, Mg, Al, and Ca.<sup>27,28</sup> For example, well-mixed probes of  $TiO_2$  and Ti powders can be converted to titanium monoxides via arc melting in an oxygen-free atmosphere at 2273 K, and in a tube furnace at 1173 K.<sup>28</sup> Various titanium monoxides have also been synthesized by heating of  $TiO_2$  powders with  $CaCl_2$  at 1373 K (ref. 25) and  $CaH_2$  at 625 K.<sup>26</sup> Geng *et al.* established the nanotube-shaped  $Ti_nO_{2n-1}$  films by Ti anodizing in the  $H_2$  atmosphere at 1323 K (ref. 29) whereas He *et al.* formed magneli phase  $Ti_8O_{15}$  nanowires with a diameter of 30 nm and a length of 2.5  $\mu m$  on a cleaned Ti substrate by heating together with  $TiO_2$  powders placed separately in a tube furnace under a  $N_2$  stream at 1323 K.<sup>30</sup> However, it is commonly accepted that  $Ti_nO_{2n-1}$  is difficult to synthesize. Firstly, processing in the oxygen-free atmosphere at high temperature is required. Secondly,  $Ti_nO_{2n-1}$  is unstable even at 425–525 °C temperatures decomposing to various superstructures.<sup>31</sup> As a result,  $Ti_nO_{2n-1}$

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materials synthesized by heating a mixture of powdered Ti and  $TiO_2$  at high temperature, usually comprised a two-phase composition. To overcome this problem, chemical,<sup>32</sup> electrochemical,<sup>33</sup> mechano-chemical,<sup>34</sup> and flame<sup>35</sup> synthesis methods of  $Ti_nO_{2n-1}$  compounds have been proposed.

Here we present a facile synthesis pathway of novel, nanoplatelet-shaped titanium monoxide film on a Ti substrate. It is worth noting that to date there are no reports of the direct formation of titanium monoxide nanoplatelet films well attached to a conductive substrate. The surprising result was obtained in this study *via* hydrothermal oxidation of a titanium substrate in a slightly alkaline selenious acid solution at a quite low temperature, *ca.* 150° to 180 °C. To explain the low bandgap value of titania films with a novel design, EPR investigations were performed.

## Materials and methods

### Materials

All of the materials were purchased from Sigma-Aldrich unless stated otherwise. Ti foil, 99.7 at% purity and 0.127 mm thick, purchased from Aldrich, was used to prepare specimens of 12 × 12 mm<sup>2</sup>. For the EPR investigations, sub-micrometer-sized Ti particles (<20 µm, 93% in water) were purchased from Alfa Aesar.

### Synthesis

The surface of Ti samples and particles was ultrasonically cleaned in acetone, ethanol, and water, for 6 min in each, etched in the solution containing  $H_2O$ ,  $HNO_3$  and HF (20%) (5 : 4 : 1 by volume) at room temperature (RT) for 10 s, well rinsed and air-dried. Nanoplatelet-shaped films on the Ti surface were synthesized as follows. At first, the pH of an aqueous solution containing 0.05 to 0.5 mol L<sup>-1</sup> of selenious acid (the highest purity, purchased from Russia) was shifted to the alkaline region by dropwise addition of 0.1 mol L<sup>-1</sup> NaOH solution and intense mixing. Then 15 mL of this solution was poured into a Teflon line stainless steel autoclave of 25 mL volume. Every Ti specimen was mounted vertically in the solution by means of a Teflon holder. For the EPR investigations, the sub-micrometer-sized Ti particles instead of Ti foil specimens were used. The synthesis was conducted at 180° for up to 48 h using a 10 °C min<sup>-1</sup> ramp. Finally, the products were carefully rinsed with distilled water and dried in air naturally. The annealing of samples was carried out in air and oxygen-free (quartz ampule with Cu foil) atmospheres at 300, 400, and 440 °C for 2 h.

### Characterization

The morphology and elemental composition of the obtained products were investigated using scanning electron microscopy FEI Quatra 200F and the Cross Beam Workstation Auriga equipped with the field emission gun and an EDX spectrometer.

X-ray powder diffraction experiments were performed with a D8 diffractometer (Bruker AXS, Germany), equipped with a Göbel mirror as a primary beam monochromator for  $CuK_\alpha$

radiation. Diffuse reflectance spectra of titania films were obtained by means of a Shimadzu UV-VIS-NIR spectrophotometer UV-3600 coupled with a MRC-3100 unit. Measurements were performed by mounting a sample holder onto the integrating sphere. The measurable range of wavelengths falls between 200 nm and 850 nm, covering the UV and visible light regions. In the integrating sphere, one beam strikes the sample normally to the surface while the other beam – aslant. The light absorbance was calculated from the diffuse reflection coefficient using the Kubelka-Munk function. X-ray photo electron spectroscopy (XPS) measurements were carried out using the ESCALAB MKII spectrometer equipped with a new XR4 twin anode. The non-monochromatic  $MgK_\alpha$ , X-ray source was operated at  $h\nu = 1253.6$  eV with 300 W power (20 mA/15 kV) and the pressure in the analysis chamber was lower than  $5 \times 10^{-7}$  Pa during spectral acquisition. The spectra were obtained using an electron analyzer with a pass energy of 20 eV for narrow scans and a resolution of 0.05 eV and with a pass energy of 100 eV for survey spectra. All spectra were recorded at a 90° take-off angle and calibrated using the C 1s peak at 284.6 eV. The spectra calibration, processing and fitting routines were done using the Advantage software (5.918) provided by Thermo VG Scientific. Core level peaks of Ti 2p, Se 3d, and O 1s were analyzed using the nonlinear Shirley-type background and the calculation of the elemental composition was performed on the basis of Scofield's relative sensitivity factors. To investigate the optical properties of titania films, the reflectance spectra of the samples were recorded in the wavelength range of 200–1700 nm using a Shimadzu UV-VIS-NIR spectrophotometer equipped with a MPC-3100 integrating sphere. The specular reflectance of the light from the film surface was calculated using an optical model of two layers. The Bruggeman Effective Medium Approximation (EMA) was applied to calculate the optical constants of the nanoplatelet titanium monoxide film formed on the Ti substrate and consisting of the naturally formed thin layer of  $TiO_2$  and the nanoplatelet titanium monoxide layer with the empty voids (see Scheme 1 in Fig. 6). The porosity of films was calculated by fitting the model functions to the measured data using a CompleteEASE software program, as in our previous study of porous alumina.<sup>36</sup>

### EPR investigations

Continuous-wave electron paramagnetic resonance (CW EPR) experiments were performed using a Bruker X-band ELEXSYS E580 EPR spectrometer. The strength and frequency of the modulating field were 0.3 mT and 100 kHz, respectively. Simulations of the CW EPR spectra were performed using EasySpin 5.2.20.<sup>37</sup>

## Results and discussion

Selenious acid ( $H_2SeO_3$ ) aqueous solutions were selected herein due to their known oxidant reactivity<sup>36</sup> through the reaction:  $H_2SeO_3 + H_2O + 4e \rightarrow Se^0 + 4OH^-$ , resulting in the subsequent oxidation of titanium and the formation of a pale yellow colored film. The annealing in the air as well as in an oxygen free



ampoule at temperatures from 300° to 450 °C for several hours resulted in an obviously darker yellow coloring. Moreover, after calcination of such films at up to 450 °C for 3 h, no obvious changes in the film morphology were detected by SEM.

Our initial investigations revealed that the expected oxidative behavior of the selenious acid towards the Ti substrate under hydrothermal conditions proceed in the 50 to 500  $\text{mmol L}^{-1}$  concentration range at the pH of 8 to 11 and at 140–190 °C temperatures. However, uniformly designed nanostructured films were formed mainly in the 0.1–0.3  $\text{mol L}^{-1}$  solutions at pH of 9. For evidence, Fig. 1 depicts the top-side SEM images of the Ti surface after autoclaving in 0.2  $\text{mol L}^{-1}$   $\text{H}_2\text{SeO}_3$  solutions, kept at the pHs of 9.0 and 10.0 at 150° and 180 °C for 15 h. As seen, just at a pH close to 9.0 the films with a novel nanoplatelet-shaped design were formed (Fig. 1a–d). More detailed investigations of these films with a SEM revealed the formation of an array from densely packed nanoplatelets of the length of 80–100 nm and the thickness of 5–12 nm (see Fig. 1b and d), depending on the pH, synthesis temperature and the processing time. It was determined that apart from the pH, the crucial role on the titania film design and the film thickness is played the autoclaving temperature. By increasing the treatment temperature from 150° to 180 °C, the average thickness of the titania layer is increased from about 80–86 nm to 240–260 nm (see insets in Fig. 1).

Under the optimized synthesis conditions (150–180 °C, 15 h), most probably due to the small thickness, the elemental composition of these films cannot be determined by the EDX analysis. X-ray photoelectron spectroscopy (XPS) analysis indicated that the as-formed films on the surface side were mainly composed of titanium and oxygen. Just a small content of selenium was detected by XPS at the film surface. An increase in the concentration of selenious acid from 0.05 to 0.5  $\text{mol L}^{-1}$  resulted in the incorporation of just somewhat larger amount of selenium. Noteworthy, at pH of 10.0 (Fig. 1f), there is an obvious difference of the as-formed film morphology because the somotoid-shaped species randomly distributing on the surface are formed. Fig. 2 depicts XRD patterns of the as-formed (a) and annealed (b) film formed on the Ti substrate by hydrothermal treatment in the  $\text{H}_2\text{SeO}_3$  solution. It can be noted that the as-formed films in the low-concentrated solution, *e.g.* 0.05–0.1  $\text{mol L}^{-1}$  for up to 30 h, were found to be composed mainly of amorphous components. In more concentrated  $\text{H}_2\text{SeO}_3$  solutions, *e.g.* 0.2–0.5  $\text{mol L}^{-1}$ , as-formed films were also found to be amorphous but containing titanium monoxide  $\text{TiO}_{0.84}$  crystallites due to the clearly resolved peak at  $2\theta$  36.92°, corresponding to the peak from the {111} plane. After annealing in the oxygen-containing atmosphere these nanoplatelet films seem to be composed of both crystalline  $\text{TiO}_2$  and nonstoichiometric titania phases (see b pattern and inset in Fig. 2). It is reasonable to note that the shift of the main XRD peak ascribed to anatase and usually seen at  $2\theta = 25.2^\circ$  to the lower angles, namely 22.6°, could be related to the formation of nonstoichiometric titania. All other experiments, performed without  $\text{H}_2\text{SeO}_3$  at the varying pH and temperature, have never shown such morphology and the  $\text{TiO}_x$  phase formation. Furthermore, no detectable peaks corresponding to Se–O or Ti–Se compounds were observed in

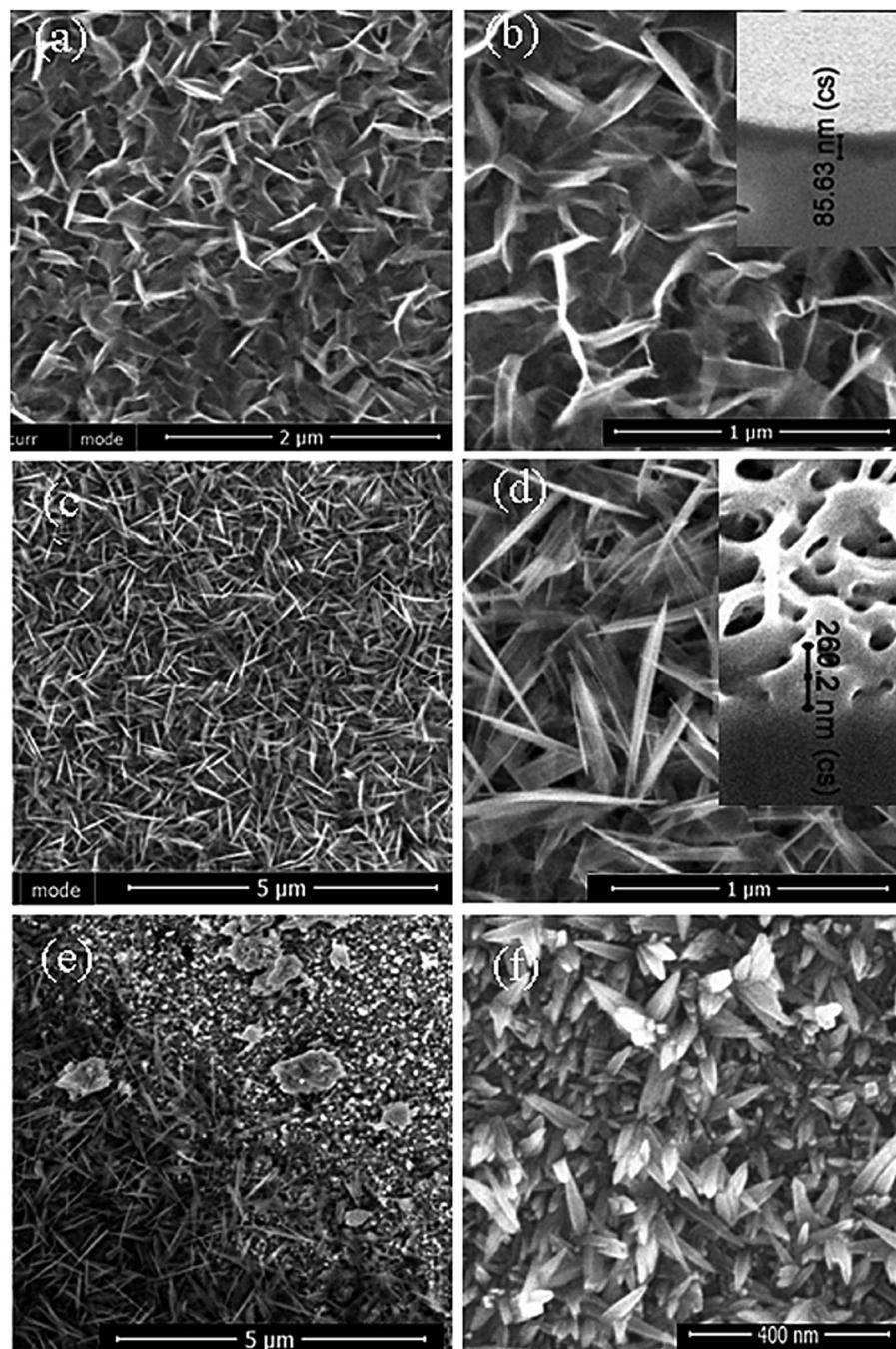
the XRD patterns of nanoplatelet films formed in the solutions containing from 0.05 to 0.5  $\text{mol L}^{-1}$  of  $\text{H}_2\text{SeO}_3$  by the hydrothermal treatment at the temperatures from 150° to 180 °C for up to 48 h.

To further explore the composition of nanoplatelet-shaped films as-formed by the hydrothermal treatment under the optimized conditions of this study and after calcination at various temperatures, investigation were conducted using CW EPR of the sub-micrometer-sized titanium particles. It is worth noticing, that in this case the quite similar morphology films were formed. Note that EPR is a precise tool to reveal the existence of  $\text{Ti}^{3+}$  and oxygen vacancies in the titania materials.<sup>38–40</sup> Fig. 3 depicts the EPR spectrum recorded at 110 K for titanium species after hydrothermal treatments in the selenious acid solutions and subsequent calcination in the oxygen-free atmosphere. The spectrum consists of two slightly overlapping signals exhibiting different saturation behavior. The narrow line at  $g = 2.0023 \pm 0.0001$  might be attributed to the conduction electrons as previously observed in anatase after thermal reduction at high temperature.<sup>41</sup> We also cannot rule out that the origin of this signal is some free radicals formed during the sample preparation. The second signal is much broader with an effective  $g$ -value of  $1.961 \pm 0.003$ , which is typical for  $\text{Ti}^{3+}$  ions in various environments and polymorphs of titania.<sup>38,40,41</sup>

X-ray photoelectron spectroscopy (XPS) investigations were carried out to determine the composition and valence states of elements involved in the nanoplatelets. In the survey spectrum (Fig. 4a), the elements of Ti, Se, and O are clearly identified. Besides the above elements, the C element was also observed most probably due to the adventitious hydrocarbon from the XPS spectrometer itself and was not further analyzed. The Ti 2p<sub>3/2</sub> peak (Fig. 4b) can be decomposed into two components centered at 459.6 and 458.5 eV, attributable to different oxidation states of titanium.<sup>42–45</sup> The main component at 458.5 eV corresponds to the  $\text{Ti}^{4+}$  state.<sup>43–45</sup> The second component at 459.6 eV probably is due to the small or Ti–OH contribution.<sup>43,44</sup> The absence of clearly resolved  $\text{Ti}^{3+}$  2p<sub>3/2</sub> binding energy in a vicinity of 456.8–457.8 eV (ref. 46 and 47) most probably should be ascribed to the formation of titanium monoxide mainly in a lower part of film not capable analyze by XPS.

Fig. 4 panel c depicts the high-resolution scans of the Se 3d electrons for the sample obtained by the hydrothermal treatment in the same  $\text{H}_2\text{SeO}_3$  solutions under the same synthesis conditions, *e.g.* 150 °C for 15 h. From the deconvoluted peak areas, Se is mainly present in the  $\text{Se}^0$ .<sup>46,47</sup> Furthermore, the incorporation of selenium was estimated to be just ~0.48, ~0.67 and ~1.1 at% for 0.1, 0.3, and 0.5  $\text{mol L}^{-1}$  solutions. Besides, the quantity of  $\text{Se}^0$  increased with the solution concentration increase from ~28% (at 0.1  $\text{mol L}^{-1}$ ) to ~33% (at 0.3  $\text{mol L}^{-1}$ ) and ~83% (at 0.5  $\text{mol L}^{-1}$ ). In addition, we have found that post-calcination of the nanoplatelet film in the oxygen-free ampoule at 350 °C results in the evaporation of elemental selenium from the titanium monoxide film sublimating onto the walls of the glass tube by drops, well confirming the incorporation of a- $\text{Se}^0$  species instead of formation the titanium selenides.





**Fig. 1** Top-side FESEM images of the  $\text{TiO}_x$  film formed on the Ti surface by hydrothermal treatment in the solution containing  $0.2 \text{ mol L}^{-1}$   $\text{H}_2\text{SeO}_3$  and  $\text{NaOH}$  up to  $\text{pH} = 9.0$  (a–e) or  $\text{pH} = 10.0$  (f) at  $150^\circ\text{C}$  (a, b and f),  $180^\circ\text{C}$  (c and d) or  $200^\circ\text{C}$  (e) for 15 h. In the insets, the cross-sectional fragments of the corresponding film are presented.

To determine the absorption coefficient and an indirect band gap characteristic of titania films, the diffuse reflectance spectra were further collected and analyzed. The absorption coefficient ( $A$ ) was calculated by the formula:  $A = (1 - R)^2/2R$ ,<sup>48</sup> where  $R$  is the reflectance. The Kubelka Munk function plots for possible indirect transitions  $[(Ahv)^{1/2} \text{ vs. } hv]$  of selected nano-platelet films fabricated under conditions of this study as a function of the subsequent annealing treatments are displayed in Fig. 5. As shown, the film synthesized at  $150^\circ\text{C}$  and

annealed in the oxygen-free atmosphere at  $350^\circ$ ,  $400^\circ$ , and  $440^\circ\text{C}$  exhibits the optical gap of 2.83, 1.74, and 2.32 eV, respectively. The strongest absorption in the visible range shows the film calcined at  $400^\circ\text{C}$ . With the further  $T_{\text{an}}$  increase to  $440^\circ\text{C}$ , the  $E_g$  value decreased to 2.32 eV, which is significantly lower than a typical  $E_g$  value of anatase  $\text{TiO}_2$  equal to  $\sim 3.2$  eV. This result can be ascribed to decomposition of titanium suboxides at  $T_{\text{an}} \geq 450^\circ\text{C}$ , as reported in ref. 49. It is worth noticing that in case of annealing the  $180^\circ\text{C}$  film in the



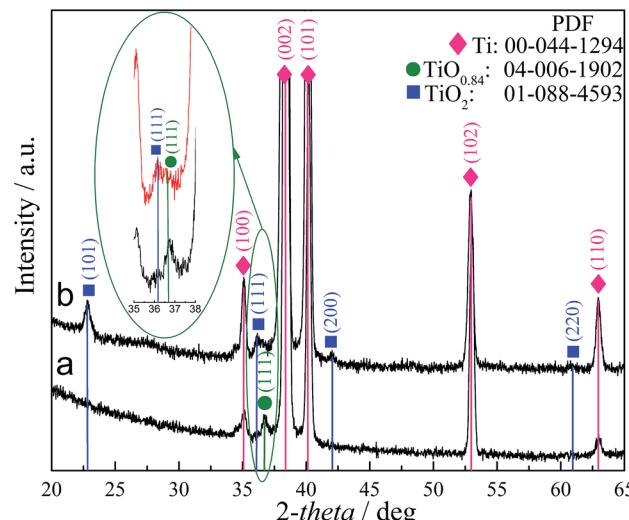


Fig. 2 XRD patterns of the film formed at the Ti substrate by hydrothermal treatment in the solution of  $0.2 \text{ mol L}^{-1} \text{H}_2\text{SeO}_3$  ( $\text{pH} = 9.0$ ) at  $150^\circ\text{C}$  for 15 h before (a) and after (b) annealing in oxygen-containing atmosphere at  $350^\circ\text{C}$  for 2 h.

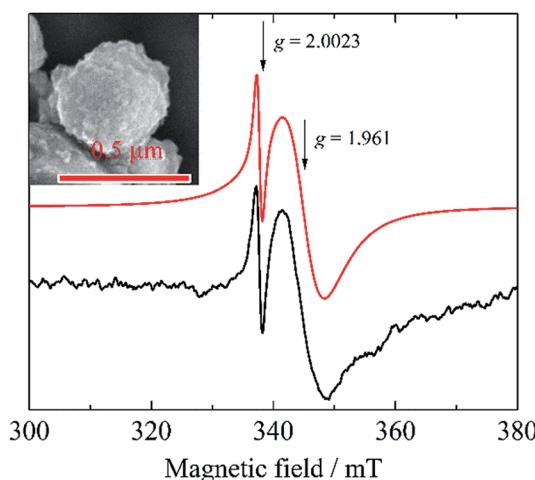


Fig. 3 Experimental (black) and simulated (red) CW EPR spectrum of titanium particles hydrothermally treated in the solution of  $0.2 \text{ mol L}^{-1}$  selenious acid at  $180^\circ\text{C}$  for 45 h. In the inset, SEM image of  $\text{TiO}_{0.84}$  coated NP.

oxygen-free atmosphere at  $400^\circ\text{C}$  the film possessing the smallest band gap value of  $1.29 \text{ eV}$  (Fig. 5b) was fabricated.

To determine the possible parameters of the nanoplatelet  $\text{TiO}_{0.84}$  film formed in the adapted herein solution under the optimized hydrothermal treatment conditions, *e.g.*  $180^\circ\text{C}$ , 15 h, before and after annealing at  $400^\circ\text{C}$  in the air and in the oxygen-free atmosphere, the model of the nanoporous titania film as in ref. 50 and 51 was developed (Fig. 6a) and analyzed. For example, Fig. 6b depicts the experimental reflection *versus* wavelength,  $R_p(\lambda)$ , plot for the nanoplatelet film calcined in the oxygen-free atmosphere. The same plot was calculated on the basis of the film model and it is presented by a red line. In this way, it was determined that the shape of the theoretically

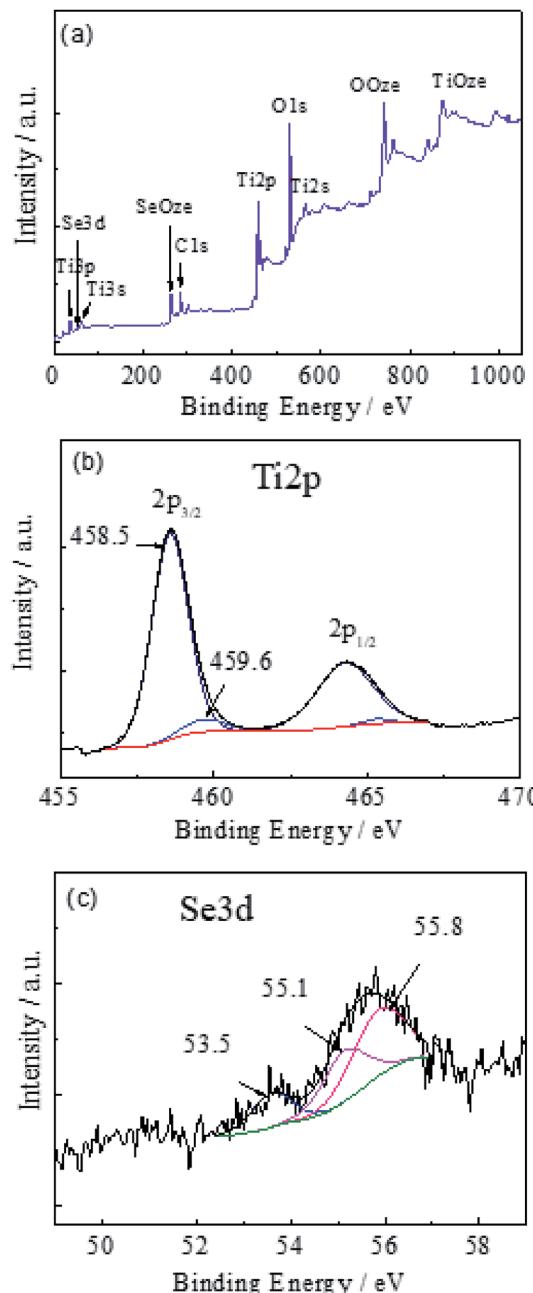


Fig. 4 Survey (a) and deconvoluted X-ray photoelectron spectra of Ti 2p (b) and Se 3d (c) elements encased at the surface side of the film formed on the Ti substrate by hydrothermal treatment in  $0.3 \text{ mol L}^{-1} \text{H}_2\text{SeO}_3$  solution ( $\text{pH} = 9.0$ ) at  $150^\circ\text{C}$  for 15 h.

calculated plot  $R_p(\lambda)$  well resembled the experimental one if the film thickness approximated  $86.6 \text{ nm}$  and the surprising 79% porosity well complying with the film structure observation by SEM presented in Fig. 1d.

It can be inferred that an increase in the band gap reduction of nanoplatelet titania could be attributed to the doping with selenium. However, the selenium content in the film is very low, not detectable by XRD and Raman (the data are not presented) and it decreases further upon calcination in the ampoule due to evaporation and sublimation of  $\text{Se}^0$  ruling out the possibility to

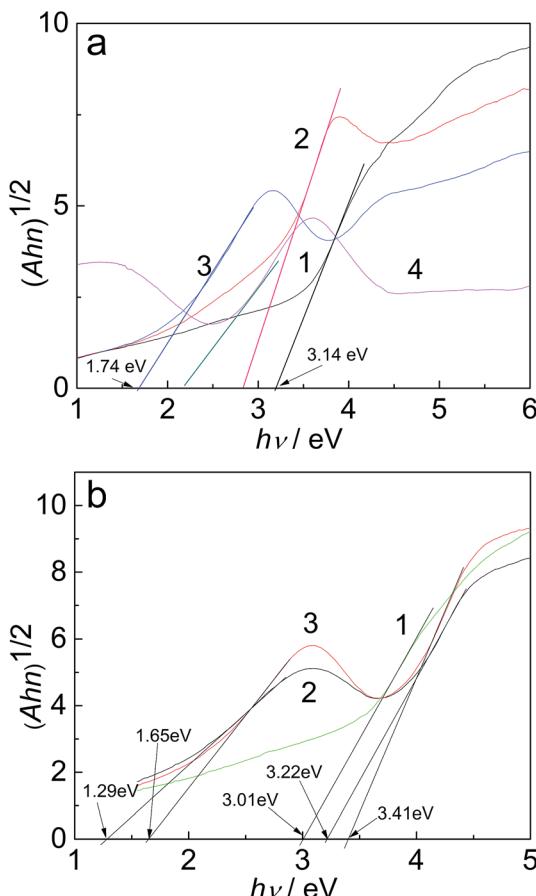


Fig. 5 (a) Tauc plots for indirect transitions of titanium monoxide nanoplatelet arrays formed by hydrothermal treatment in the  $0.3 \text{ mol L}^{-1} \text{H}_2\text{SeO}_3$  solution ( $\text{pH} = 9.0$ ) at  $150 \text{ }^\circ\text{C}$  for 15 h after calcination in the air (1) and oxygen-free atmosphere at: 350 (2); 400 (3), and  $440 \text{ }^\circ\text{C}$  (4) for 2 h. In (b), the same plots for the film grown at  $180 \text{ }^\circ\text{C}$  for 15 h after calcination in air (1) and oxygen-free atmosphere at  $400 \text{ }^\circ\text{C}$  (2) and  $440 \text{ }^\circ\text{C}$  (3) for 2 h.

increase the band gap redshift. To check the influence of  $\text{Se}^0$  incorporation, the nanotubed titania ( $\text{TiNt}$ ) films decorated with  $\text{Se}^0$  nanoparticles were further designed and their optical

properties were investigated. For this purpose, Ti specimens were anodized in the ethylene glycol solution containing  $\text{NH}_4\text{F}$  and  $\text{H}_2\text{O}$  at 50 V for 30 min as previously reported<sup>14</sup> and calcined in the air at  $450 \text{ }^\circ\text{C}$  for 2 h. In this way, the nanotube shaped (Fig. 7a) film of the  $4.7 \mu\text{m}$  thickness with  $120 \text{ nm}$  tubes at the metal|film interface was formed. For crystallization, the samples were annealed at  $450 \text{ }^\circ\text{C}$  in the air for 2 h ( $\partial T/\partial t = 10 \text{ }^\circ\text{C min}^{-1}$ ). The decoration of this film with  $\text{Se}^0$  was carried out by electrodeposition from the  $0.2 \text{ mol L}^{-1} \text{H}_2\text{SeO}_3$  solution as in the case of alumina.<sup>52</sup> As seen from the Se mapping image (Fig. 7b) and the Se distribution in the film cross-section (Fig. 7c), the adapted herein treatment conditions result in the rather uniform deposition of selenium species through all the film thickness. Furthermore, the Raman spectra (Fig. 7d) revealed deposition of pure  $\text{Se}^0$  species, whereas the XRD pattern (not shown herein) indicated their amorphous nature. Eventually, the diffuse reflectance spectra for several films with various  $\text{Se}^0$  contents were investigated and characteristic plots (Fig. 7e) were analyzed. As can be seen, the heterostructuring of titania nanotubes with a- $\text{Se}$  species only slightly redshifts the band gap of anatase  $\text{TiO}_2$ . These results well comply with the reported ones.<sup>53</sup> Therefore, a significant  $E_g$  redshift of our nanoplatelet films should be mainly ascribed to the formation of the low band gap titanium monoxide family member  $\text{TiO}_{0.84}$  confirmed by XRD and EPR.

## Conclusions

Herein we demonstrated a simple possibility of forming a low band gap nanoplatelet species array on a Ti substrate by hydrothermal synthesis and a subsequent calcination. For this purpose, selenious acid solutions kept at a pH close to 9.0 were successfully used for the first time. The current study shows that the nanoplatelet shaped film, of a thickness up to  $250 \text{ nm}$  formed under the optimized hydrothermal treatment conditions of this study, is mainly composed of semiconducting titanium monoxide  $\text{TiO}_{0.84}$  with an indirect optical band gap value as low as  $1.29 \text{ eV}$ . The nanotube-shaped anatase  $\text{TiO}_2$  film decorated with  $\text{Se}^0$  species was

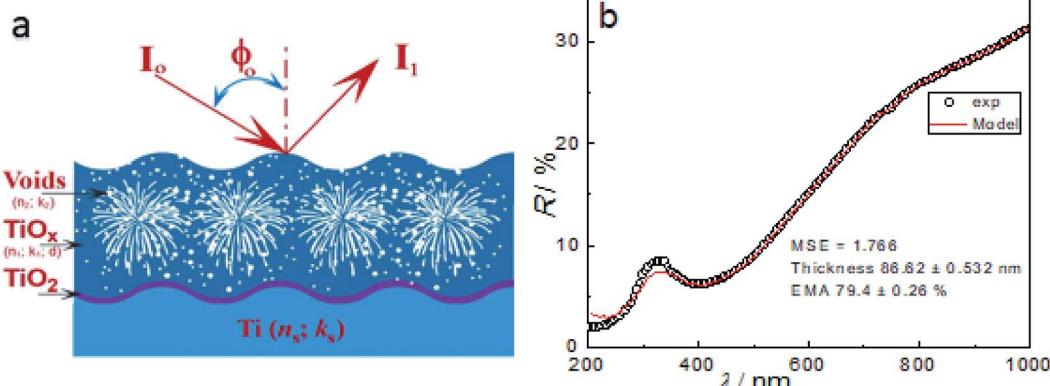


Fig. 6 (a) The scheme corresponding to the model used for the fitting of experimental  $R(\lambda)$  dependency. In (b) the reflection vs. wavenumber ( $\lambda$ ) plots for experimental  $180 \text{ }^\circ\text{C}$   $\text{TiO}_{0.84}$  film (circles) and the calculated one (line) by the adapted nanoporous film model.

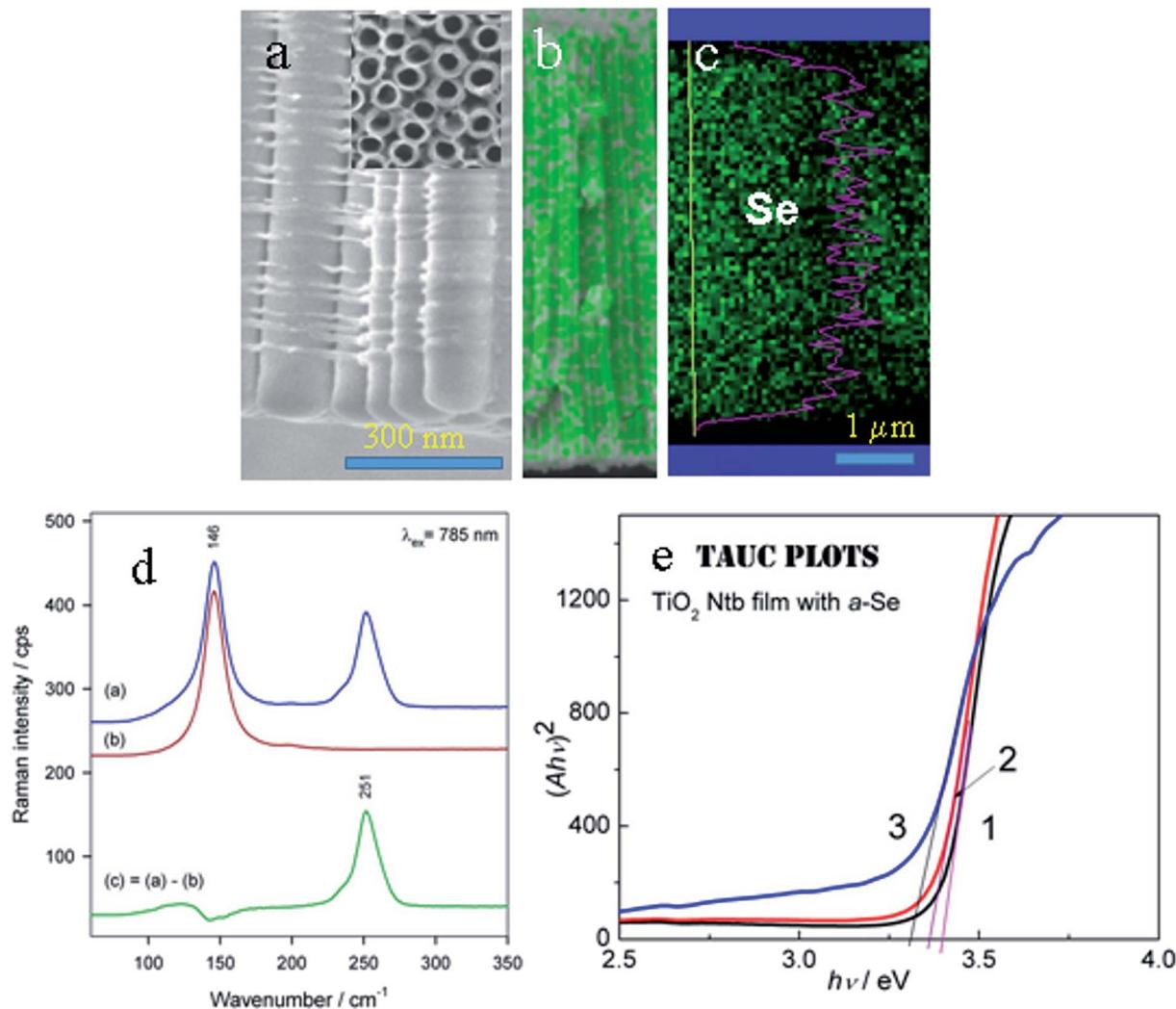


Fig. 7 Panoramic (a), top-side (inset), and cross-sectional (b) SEM views of anatase  $\text{TiO}_2$  film fabricated by Ti anodizing in the ethylene glycol solution containing 0.25  $\text{NH}_4\text{F}$  and 1.0 wt%  $\text{H}_2\text{O}$  at 50 V for 30 min followed by calcination at 450  $^{\circ}\text{C}$  for 2 h before (a) and after the Se DC deposition in 0.005 mol  $\text{L}^{-1}$   $\text{H}_2\text{SeO}_3$  solution at  $-2.0$  V for 5 min (b). In (c) the element map and distribution profile of the Se species encased inside the film across all the  $\text{TiO}_2$  film thickness ca. 4.75  $\mu\text{m}$ . In (d) the Raman spectra of TiNt/Se (a), pure TiNt (b) and difference (c). In (e) the Tauc plots of TiNt film before (1) and after DC deposition of a-Se at 1.5 V for 2 (2) and 7 (3) min.

also designed and studied herein. The comparison of its optical properties with the those of our film implied that the significant  $E_g$  redshift of our nanoplatelet films should be ascribed to the formation of the low band gap titanium monoxide family member  $\text{TiO}_{0.84}$  confirmed by XRD and EPR. We suppose that these nanotechnology-driven titania films could have an indispensable potential to discover novel sensor devices in the future.

## Author contributions

A. J. designed, supervised and managed the study. S. R. performed syntheses and morphological characterization of the products. The XPS, and EPR investigations were carried out by V. J. and M. Š., respectively. All authors have given approval to final version of the manuscript.

## Conflicts of interest

The authors declare no competing financial interest and any unpaid roles or relationships that might have a bearing on the publication process.

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