Introduction

Titanium dioxide, TiO₂, 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, nontoxic and simple processing at a low cost. The crystalline forms of TiO₂—anatase, TiO₂-rutile and TiO₂-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, photocatalysis, solar cell devices, photo catalysis, batteries, etc. For example, the presence of vacancies in TiO₁₀ results in an $E_g \approx 2.0$ eV, as reported by Gusev.³ To date different precursors and synthesis methods have been reported for Ti₁O₂ₙ₋₁ and TiO₂ fabrication.²³–²⁸ From these reports, titanium monoxides can be synthesized from raw TiO₂ powders by high temperature reduction with hydrogen,₂² carbon₂₅–₂₆ and active metals such as Ti, Na, Ca, Mg, Al, and Ca.²₇–²₈ For example, well-mixed probes of TiO₂ 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.²⁸ Various titanium monoxides have also been synthesized by heating of TiO₂ powders with CaCl₂ at 1373 K (ref. 25) and CaH₂ at 625 K. Geng et al. established the nanotube-shaped Ti₁O₂ₙ₋₁ films by Ti anodizing in the H₂ atmosphere at 1323 K (ref. 29) whereas He et al. formed magneli phase Ti₁O₁₅ nanowires with a diameter of 30 nm and a length of 2.5 μm on a cleaned Ti substrate by heating together with TiO₂ powders placed separately in a tube furnace under a N₂ stream at 1323 K.³₀ However, it is commonly accepted that Ti₁O₂ₙ₋₁ is difficult to synthesize. Firstly, processing in the oxygen-free atmosphere at high temperature is required. Secondly, Ti₁O₂ₙ₋₁ is unstable even at 425–525 °C temperatures decomposing to various superstructures.³¹ As a result, Ti₁O₂ₙ₋₁

Hydrothermal synthesis and characterization of nanostructured titanium monoxide films

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At the present time, the formation of titanium monoxide (TiO₁) two dimensional (2D) species with distinct composition, size, shape, and a significantly reduced bandgap ($E_g$) value compared to TiO₂ is of great scientific and practical importance. This paper describes our findings investigating Ti surface oxidation for the formation of TiO₁ 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 TiO₂ porous films was created by this method for the first time. The formation of titanium monoxide, particularly TiO₁₀.₈₄, 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 μm exhibited a very large shift of their light absorption threshold, down to 1.29 eV, compared to the $E_g$ of anatase TiO₂ and a surprising 70% porosity determined via simulation of experimental reflection plots. It is anticipated that this unique TiO₁ nanomaterial will pave the way for new investigations and applications.

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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,\textsuperscript{12} electro-
chemical,\textsuperscript{13,14} mechano-chemical,\textsuperscript{14} and flame\textsuperscript{15} synthesis 
methods of Ti$_2$O$_{2m-1}$ 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$^\circ$C to 180$^\circ$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 
otherwise stated. Ti foil, 99.7 at% purity and 0.127 mm thick, 
purchased from Aldrich, was used to prepare specimens of 12 $\times$ 
12 mm$^2$. For the EPR investigations, sub-micrometer-sized Ti 
particles ($<$20 $\mu$m, 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$_2$O, 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$^{-1}$ of selenious 
acid (the highest purity, purchased from Russia) was shifted to 
the alkaline region by dropwise addition of 0.1 mol L$^{-1}$ 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$^\circ$C for up to 48 h 
using a 10$^\circ$C min$^{-1}$ 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$^\circ$C for 2 h.

Characterization

The morphology and elemental composition of the obtained 
products were investigated using scanning electron microscopy 
FEI Quatro 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 ob-
tained 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 absorb-
ance was calculated from the diffuse reflection coefficient 
using the Kubelka-Munk function. X-ray photo electron spec-
troscopy (XPS) measurements were carried out using the 
ESCALAB MKII spectrometer equipped with a new XRF twin 
anode. The non-monochromatic MgK$_\alpha$ X-ray source was oper-
ated 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$^\circ$ take-off angle 
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 Sco-
field’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.\textsuperscript{26}

EPR investigations

Continuous-wave electron paramagnetic resonance (CW EPR) 
experiments were performed using a Bruker X-band ELEXYS 
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.\textsuperscript{37}

Results and discussion

Selenious acid (H$_2$SeO$_3$) aqueous solutions were selected herein 
due to their known oxidant reactivity\textsuperscript{28} through the reaction: 
H$_2$SeO$_3$ + H$_2$O + 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 selenium acid towards the Ti substrate under hydrothermal conditions proceed in the 50 to 500 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 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 mol L⁻¹ H₂SeO₃ solutions, kept at the pHs of 9.0 and 10.0 at 150 °C 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 formation of an array from densely packed nanoplatelets of the thickness 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 °C 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 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 somatoid-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 H₂SeO₃ solution. It can be noted that the as-formed films in the low-concentrated solution, e.g. 0.05–0.1 mol L⁻¹ for up to 30 h, were found to be composed mainly of amorphous components. In more concentrated H₂SeO₃ solutions, e.g. 0.2–0.5 mol L⁻¹, as-formed films were also found to be amorphous but containing titanium monoxide TiO₀.₄₄ crystalitles due to the clearly resolved peak at 2θ 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 TiO₂ 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 2θ = 25.2° to the lower angles, namely 22.6°, could be related to the formation of nonstoichiometric titania.

All other experiments, performed without H₂SeO₃ at the varying pH and temperature, have never shown such morphology and the TiO₂ 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 mol L⁻¹ of H₂SeO₃ 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 Ti³⁺ and oxygen vacancies in the titania materials. 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 ± 0.0001 might be attributed to the conduction electrons as previously observed in anatase after thermal reduction at high temperature. 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 ± 0.003, which is typical for Ti⁴⁺ ions in various environments and polymorphs of titania.

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 2p₁/₂ peak (Fig. 4b) can be decomposed into two components centered at 459.6 and 458.5 eV, attributable to different oxidation states of titanium. The main component at 458.5 eV corresponds to the Ti⁴⁺ state. The second component at 459.6 eV probably is due to the small or Ti–OH contribution. The absence of clearly resolved Ti³⁺ 2p½ 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 H₂SeO₃ solutions under the same synthesis conditions, e.g. 150 °C for 15 h. From the deconvoluted peak areas, Se is mainly present in the Se⁰. 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 mol L⁻¹ solutions. Besides, the quantity of Se⁰ increased with the solution concentration increase from ~28% (at 0.1 mol L⁻¹) to ~33% (at 0.3 mol L⁻¹) and ~83% (at 0.5 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-Se⁰ species instead of formation the titanium selenides.
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: $A = (1 - R)^2/2R$, where $R$ is the reflectance. The Kubelka Munk function plots for possible indirect transitions ($[A\hbar\nu]^{1/2}$ vs. $\hbar\nu$) of selected nanoplatelet 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 °C and annealed in the oxygen-free atmosphere at 350°, 400°, and 440 °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 °C. With the further $T_{an}$ increase to 440 °C, the $E_g$ value decreased to 2.32 eV, which is significantly lower than a typical $E_g$ value of anatase TiO$_2$ equal to ~3.2 eV. This result can be ascribed to decomposition of titanium suboxides at $T_{an} \approx 450$ °C, as reported in ref. 49. It is worth noticing that in case of annealing the 180 °C film in the...
The film possessing the smallest band gap value of 1.29 eV (Fig. 5b) was fabricated. To determine the possible parameters of the nanoplatelet TiO$_{0.84}$ film formed in the adapted herein solution under the optimized hydrothermal treatment conditions, e.g. 180 °C, 15 h, before and after annealing at 400 °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 calculated plot $R_p(\lambda)$ well resembled the experimental one if the film thickness approximated 86.6 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 Se ruling out the possibility to...

**Fig. 2** XRD patterns of the film formed at the Ti substrate by hydrothermal treatment in the solution of 0.2 mol L$^{-1}$ H$_2$SeO$_3$ (pH = 9.0) at 150 °C for 15 h before (a) and after (b) annealing in oxygen-containing atmosphere at 350 °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 mol L$^{-1}$ selenious acid at 180 °C for 45 h. In the inset, SEM image of TiO$_{0.84}$ coated NP.

**Fig. 4** Survey (a) and deconvoluted X-rays 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 mol L$^{-1}$ H$_2$SeO$_3$ solution (pH = 9.0 ) at 150 °C for 15 h.
increase the band gap redshift. To check the influence of Se\textsuperscript{0} incorporation, the nanotubed titania (TiNt) films decorated with Se\textsuperscript{0} nanoparticles were further designed and their optical properties were investigated. For this purpose, Ti specimens were anodized in the ethylene glycol solution containing NH\textsubscript{4}F and H\textsubscript{2}O\textsubscript{2} at 50 V for 30 min as previously reported\textsuperscript{14} and calcined in the air at 450 °C for 2 h. In this way, the nanotubed shaped (Fig. 7a) film of the 4.7 µm thickness with 120 nm tubes at the metal/film interface was formed. For crystallization, the samples were annealed at 450 °C in the air for 2 h (\(\frac{dT}{dt} = 10 ^{\circ} \text{C min}^{-1}\)). The decoration of this film with Se\textsuperscript{0} was carried out by electrodeposition from the 0.2 mol L\textsuperscript{-1} H\textsubscript{2}SeO\textsubscript{3} solution as in the case of alumina.\textsuperscript{52} 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 Se\textsuperscript{0} species, whereas the XRD pattern (not shown herein) indicated their amorphous nature. Eventually, the diffuse reflectance spectra for several films with various Se\textsuperscript{0} contents were investigated and characteristic plots (Fig. 7e) were analyzed. As can be seen, the heterostructuring of titania nanotubes with a-Se species only slightly redshifts the band gap of anatase TiO\textsubscript{2}. These results well comply with the reported ones.\textsuperscript{53} 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 TiO\textsubscript{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 nm formed under the optimized hydrothermal treatment conditions of this study, is mainly composed of semiconducting titanium monoxide TiO\textsubscript{0.84} with an indirect optical band gap value as low as 1.29 eV. The nanotubeshaped anatase TiO\textsubscript{2} film decorated with Se\textsuperscript{0} species was
also designed and studied herein. The comparison of its optical properties with 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 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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