


 Cite this: *RSC Adv.*, 2026, 16, 8658

Impact of variations in ALD procedure on nanomorphology, protecting properties and chemical stability of thin TiO₂ films

 Hana Krýsová,^a Tomáš Imrich,^b Hana Tarábková,^{a*} Pavel Janda^a and Josef Krýsa^{b*}

Thin TiO₂ films were deposited by atomic layer deposition (ALD) at 150 and 250 °C on FTO and Si/SiO₂ substrates to examine the effect of deposition conditions on morphology, structure, chemical stability, and photoelectrochemical performance. Films grown at 150 °C were amorphous and crystallised into anatase after annealing at 500 °C, accompanied by nanoscale morphological rearrangement. In contrast, films deposited at 250 °C were amorphous and non-stoichiometric (TiO_{2-x}) with Ti³⁺ self-doping; annealing reduced the doping level without inducing crystallisation. The films degraded in 0.1 M HClO₄ within 72 h but remained stable in alkaline media (pH 8). Electrochemical studies using the [Fe(CN)₆]^{3-/4-} redox couple showed that low-temperature ALD TiO₂ layers (8–50 nm) effectively blocked charge transfer, whereas this approach was unsuitable for high-temperature ALD films due to self-doping. The as-deposited high-temperature ALD TiO₂/FTO exhibits higher photoelectrochemical (PEC) efficiency than low-temperature films due to Ti³⁺ self-doping. The as-deposited low-temperature ALD TiO₂/FTO shows negligible PEC efficiency, which increases significantly after annealing owing to the formation of the anatase phase.

 Received 15th December 2025
 Accepted 1st February 2026

DOI: 10.1039/d5ra09703g

rsc.li/rsc-advances

Introduction

Surface coverage by thin films for the improvement of mechanical, optical, and electrochemical properties of solid surfaces is of great technological importance. In this context, corrosion, which is an electrochemical process, represents one of the concerns. If not properly protected, in an oxidizing and humid atmosphere, disintegration of metallic structural elements into oxides takes place. Protection of semiconductors against corrosion and photocorrosion in liquid media represents another important research topic.^{1–4} In photoelectrochemical applications of semiconductors, light-generated charge carriers can lead to decomposition of the material. One way of protecting a semiconductor in contact with a liquid is to cap it with a thin film, such that front side illumination is not attenuated. Insulating or wide-bandgap semiconducting oxides such as titanium dioxide are preferred as capping layer materials. Regarding a suitable deposition technique, atomic layer deposition (ALD) is the only method that enables homogeneous, pinhole free, continuous, and conformal coating of complex, three-dimensional substrates.⁵

Recently, titanium dioxide overlayer prepared by the ALD coating technique (deposition temperature 150 °C) has been investigated with the aim to protect a semiconducting hematite electrode against corrosion and photocorrosion.^{6–8} Depending on the thickness of the protecting TiO₂ layer, the passage of electrical current was progressively hindered as the layer thickness was increased from 2 to 8 nm. Such behavior was explained by the non-favourable valence band positions of hematite and titania.⁶ Moehl *et al.* investigated ALD TiO₂ protective overlayers for light absorbers in photoelectrochemical water-splitting devices, where fluorine-doped SnO₂ (FTO) was used as a model substrate.⁹ ALD deposition was performed at temperatures 120 and 150 °C, such overlayers need at least 40–60 nm thickness to be “completely blocking”. Thin, compact semiconductor TiO₂ layer deposited directly on the FTO glass, underneath the mesoporous TiO₂ layer is also an important part of dye sensitised solar cell (DSSC). Annealing step (450–550 °C, 30–60 min) in fabrication of DSSC is necessary to (i) remove organic binders, (ii) improve interparticle connectivity and (iii) improve crystallinity and phase stability.^{10,11}

Beside blocking properties chemical stability of protective overlayers is also important. Recently we have investigated in detail ALD Al₂O₃ films and found that these films rapidly dissolved in 1 M NaOH (≈ 100 nm h⁻¹). The dissolution in 1 M H₂SO₄ was slower (1 nm h⁻¹) but after 24 h the blocking behaviour was entirely lost. The optimal stability was reached at

^aJ. Heyrovský Institute of Physical Chemistry of the Czech Academy of Sciences, Dolejškova 2155/3, 182 23, Prague 8, Czech Republic. E-mail: hana.tarabkova@jh-inst.cas.cz

^bDepartment of Inorganic Technology, University of Chemistry and Technology, Technická 5, 166 28, Prague 6, Czech Republic. E-mail: josef.krýsa@vscht.cz



pH 7.2 where no changes were found up to 24 h and even after 168 h of exposure the changes in the blocking behaviour were still minimal.¹² Wang¹³ reported, that ALD TiO_x coatings significantly enhanced corrosion resistance and electrical characteristics of titanium proton exchange membrane (PEM) based water electrolyzers.

Several studies^{14–17} investigated influence of ALD process temperature, type of precursors and substrate on mechanism of TiO₂ growth and crystallinity. For atomic layer deposition of TiO₂ various precursors exist,¹⁷ most commonly used are titanium tetrachloride (TiCl₄), titanium isopropoxide (Ti [OCH(CH₃)₂]₄) and tetrakis(dimethylamino)titanium (TDMAT) in combination with ozone, O₂ or Ar–O₂ plasma and H₂O as oxidants. TDMAT has the advantage that precursor and decomposition products are non-toxic and non-corrosive.^{18,19}

The aim of the present study was to look how different ALD deposition procedures using TDMAT and H₂O as precursors and following annealing step influence morphology of thin TiO₂ layers, phase composition, and chemical stability in alkaline and acidic pH, as well as their (photo)electrochemical behavior, which are properties essential for their application as protective overlayers.

Experimental

Atomic layer deposition (ALD) was carried out using a thermal-mode ALD R-200 system (Picosun, Finland) with varying numbers of identical deposition cycles. Two ALD procedures were used for preparation of TiO₂ films using tetrakis(dimethylamido)titanium(IV) (TDMAT from Strem Chemicals, USA) and water (EpiValence, UK) as precursors with different pulse-purge sequence.²⁰ TDMAT was heated to 85 °C, and water was maintained at 22 °C. Nitrogen (99.999%) was used as the carrier gas. The processing temperatures were 150 °C for low temperature TiO₂ films (LT-ALD TiO₂) and 250 °C for the high temperature TiO₂ films (HT-ALD TiO₂), respectively. Layer thickness was controlled by the number of ALD deposition cycles and determined by ellipsometry²⁰ or AFM profile analysis of a step formed on a Si/SiO₂ substrate following removal of the TiO₂ film by scratching (Fig. S1 in SI). For post annealing, the films were calcined for 1 h in air at 500 °C, the heating ramp was 10 °C min⁻¹. Annealing conditions were selected with aim to form anatase crystalline structure and due to possible application in DSSC. Fluorine-doped tin oxide coated 2 mm thick glass ("FTO", 7 Ω □⁻¹), obtained from Merck (Germany) and an Si/SiO₂ (300 nm) wafer (Silicon Quest International, USA), were used as substrates. Substrates were cleaned using ethanol, acetone and isopropyl alcohol before deposition procedure.

X-ray photoelectron spectroscopy (XPS) measurements were performed using an ESCA Probe P spectrometer (Omicron Nanotechnology Ltd, Germany) equipped with a monochromatic Al K α radiation source (1486.7 eV). The measurements were carried out under ultra-high vacuum conditions (base pressure $\sim 5 \times 10^{-10}$ mbar). To compensate for surface charging during the analysis, a low-energy electron flood gun was employed. For spectral acquisition, a pass energy of 50 eV

with a step size of 0.4 eV was used for survey spectra, while high-resolution spectra of C 1s, O 1s, and Ti 2p were recorded with a pass energy of 30 eV and a step size of 0.1 eV. All binding energies were calibrated with respect to the C 1s peak at 284.8 eV. The instrument was calibrated using reference binding energies of Cu 2p_{3/2} (932.7 eV) and Ag 3d_{5/2} (368.26 eV), with respective full width at half maximum values of 0.85 eV and 0.67 eV. Data processing and peak fitting were performed using CasaXPS software (ver. 2.3.17PR1.1), applying Shirley background subtraction and a Gaussian–Lorentzian (GL(30)) peak shape function.

X-ray diffraction (XRD) patterns were recorded using an X'Pert Philips MPD diffractometer (The Netherlands) equipped with a PANalytical X'Celerator detector (PIXcel1D, 1D mode) and operated with Cu K α radiation ($\lambda = 1.54060$ Å) generated at 40 kV and 30 mA. Measurements were performed in continuous scan mode over the 2θ range of 5.0–90.0° with a step size of 0.039° and a scan time of 175 s per step. The goniometer radius was 240 mm, and the specimen length was 10 mm. A fixed divergence slit (1.0°) was used, and no spinning or incident beam monochromator was applied. Data analysis and phase identification were carried out using the HighScore Plus software (ver. 5.1.0.29607).

The morphology of the films was characterized by atomic force microscopy (AFM, Dimension Icon, Bruker, USA) in semi-contact (tapping TM) or peak force quantitative nano-mechanical (PFQNM) mode. A silicon VTESPA-300 cantilever with a resonant frequency, f_{res} , of approx. 300 kHz, a spring constant, k , of 42 N m⁻¹, a nominal tip radius of 5 nm (Bruker, USA) and SCANASYST-AIR cantilever, with a resonant frequency, f_{res} , of approx. 65 kHz, a spring constant, k , of 0.4 N m⁻¹, and a nominal tip radius of 2 nm (Bruker, USA) were employed for TM and PFQNM, respectively. The Gwyddion software (ver. 2.53) was used for processing AFM image data and for calculation of the roughness factor (R_f), which represents the ratio between the three-dimensional surface area of the image and its two-dimensional footprint area. The Raman spectra were measured by the MicroRaman system (WITec Alpha 300 R spectrometer, Oxford Instruments) with a Confocal microscope. The spectra were excited by a 532 nm excitation laser.

The blocking properties of the deposited layers were evaluated by cyclic voltammetry (CV) in an aqueous electrolyte composed of 0.5 mM K₃[Fe(CN)₆] and 0.5 mM K₄[Fe(CN)₆] in 0.5 M KCl pH 2.5 (pH value was adjusted by HCl). Electrochemical experiments were carried out in a one-compartment three-electrode cell using Zahner Zennium X workstation (Zahner-Elektrik, Germany) and Autolab PGSTAT 101 potentiostat (Metrohm, The Netherlands) controlled by the NOVA software.

For dissolution studies, TiO₂ films were exposed to 0.1 M HClO₄, and 0.1 M phosphate buffer solution (pH 8) for 72 h. Long term stability of film was studied in 1 M NaOH, 1 M H₂SO₄ and 0.1 M phosphate buffer (pH 7).

The determination of the titanium concentration in solution was carried out by inductively coupled plasma spectrometry (ICP-OES) using an Optima 8000 instrument (PerkinElmer, USA).



For photoelectrochemical measurements of the incident photon to current conversion efficiency (IPCE) spectra, an Electrochemical Photocurrent Spectra CIMPS-pcs system (Zahner-Elektrik, Germany) with a TLS03 tunable light source was used. The three-electrode system with the TiO₂-coated FTO working electrode, Ag/AgCl (3 M KCl) reference electrode and platinum rod as a counter electrode in 0.1 M Na₂SO₄ (pH 10) electrolyte solution was used for photoelectrochemical experiments. The TiO₂ films were illuminated from the front side (EE interface).

Results and discussion

Physical characterization

Two types of TiO₂ thin films were deposited by Atomic Layer Deposition (ALD), at lower deposition temperature 150 °C (LT-ALD TiO₂) and higher deposition temperature 250 °C (HT-ALD TiO₂). Two different ALD procedures were selected based on the initial assumption that deposition at 150 °C formed amorphous¹⁷ TiO₂, whereas the crystalline form¹⁶ of TiO₂ can be obtained at process temperature 250 °C. Fig. 1 shows the X-ray diffractograms of ALD TiO₂ films, where cassiterite lines originated from FTO substrate. XRD confirms that as-deposited LT-ALD TiO₂ film is amorphous, but annealing at 500 °C/1 h in air causes crystallization towards anatase (Fig. 1A and B). The intensity of the strongest anatase diffraction line does not increase after annealing at 500 °C for 2 h, indicating that 1 h of annealing is sufficient for complete anatase formation in the TiO₂ film. Although Chiappim *et al.*¹⁶ reports the formation of anatase crystalline phase at ALD process temperature in the range 250–300 °C, the XRD (Fig. 1C and D) indicates that HT-ALD deposition method did not result in the formation of any crystalline phase, even after post-annealing at 500 °C. The poor crystallization tendency of TiO₂ films deposited by ALD using alkylamide-based precursors at processing temperature 200–260 °C was also previously reported.¹⁷ The crystallization of the



Fig. 2 Photography of as-deposited (A and C) and annealed (B and D) 50 nm TiO₂ layers on FTO support. (A) As-deposited LT-ALD TiO₂; (B) annealed LT-ALD TiO₂; (C) as-deposited HT-ALD TiO₂; (D) annealed HT-ALD TiO₂.

TiO₂ films was found to be dependent on film thickness and impurity content, but effect of impurities on the crystallization behavior could only be observed for very thin films (<30 nm).²¹ Abendorth¹⁸ reported, that TiO₂ crystallization temperature was also dependent on H₂O purge times. The plausible explanation of the finding, that HT-ALD deposition method leads to formation of amorphous TiO₂ even after post-annealing at 500 °C remains so far unknown and is not within the scope of this paper.

Fig. 2 shows photo images of 50 nm TiO₂/FTO electrodes. While as deposited and annealed LT-ALD TiO₂ films are rather transparent (Fig. 2A and B), as-deposited HT-ALD TiO₂ has dark brown color (Fig. 2C), which is typical for reductively doped TiO₂.^{23–25}

XPS spectra of HT-TiO₂ as-deposited and after annealing at 500 °C/1 h are shown in Fig. 3. We can see that XPS analysis confirmed self-doped sites with oxygen vacancies such as Ti³⁺ (around 5%) and other low-valent Ti (around 2% of Ti²⁺) in as-deposited film (Fig. 3A). Therefore, HT-ALD deposition method forms non-stoichiometric TiO_{2-x}. The presence of Ti³⁺ in ALD grown amorphous TiO₂ was reported by Saari *et al.*²⁶ The decrease of oxygen to titanium ratio ([O]/[Ti]) with increasing deposition temperature was also observed by Kim *et al.*¹⁵ Annealing at 500 °C/1 h in air causes thermal re-oxidation of Ti(III) and Ti(II) to Ti(IV), which is confirmed by XPS analysis (Fig. 3B). The decrease in the level of doping is indicated by the change of HT-ALD TiO₂ film color from brown to yellowish (Fig. 2D).

Nanomorphology of TiO₂/FTO films was characterized by AFM (Fig. S2 in SI). Both as deposited and annealed samples do not show significant difference in nanomorphology and roughness factor. Their nanomorphology however differs from bare FTO support (Fig. S2E in SI), clearly indicating presence of deposited TiO₂ films. Table S1 (in SI) summarizes roughness factors for as-deposited LT-ALD TiO₂ films at the FTO substrate

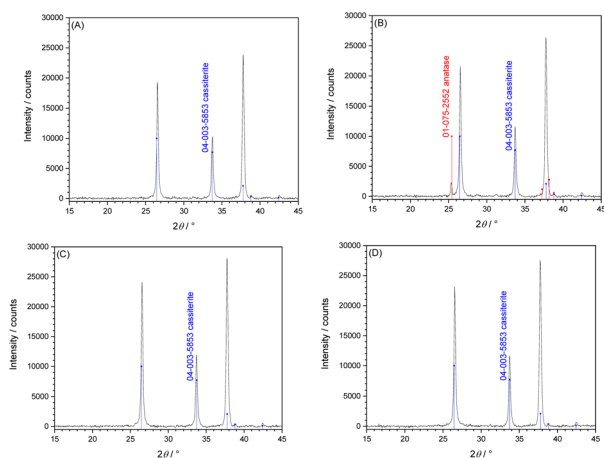


Fig. 1 XRD of 50 nm TiO₂ (ALD) layers on FTO/glass, (A) and (C) as-deposited, (B) and (D) annealed at 500 °C for 1 h in air. Deposition at 150 °C LT-ALD (A and B) and 250 °C HT-ALD (C and D). XRD reference lines: 04-003-5853 (cassiterite) and 01-075-2552 (anatase).²²

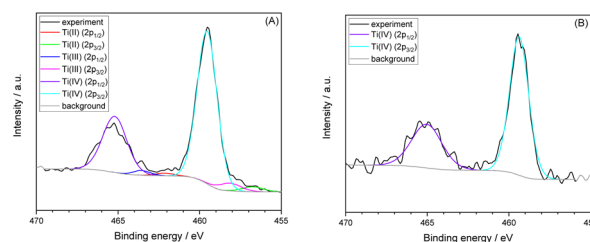


Fig. 3 XPS spectra of HT-TiO₂ as deposited (A) and after annealing at 500 °C/1 h (B). The envelope curve is not included in the figures, as it significantly overlapped with the fitted components and made their individual contributions indistinguishable.



for varying film thicknesses between 8 and 50 nm. There is no significant difference in R_f compared to bare FTO, but for 50 nm thick TiO_2 film R_f slightly decreases. We can assume conformal coverage of FTO for all our TiO_2 films, which is also evidenced by AFM height density distributions (Fig. S3 in SI).

As the FTO support has quite rough surface, the atomic force microscopy resolution is rather limited. Consequently, the application of well-defined flat substrate, such Si/SiO₂ wafer is needed for detailed high-resolution study of nanomorphology of ALD-TiO₂ thin film (Fig. 4). Apparently as deposited LT-TiO₂ films (Fig. 4A) are amorphous, conformal to SiO₂ nanomorphology (Fig. 4E), whereas annealed LT-TiO₂ films form crystalline nanodomains with visible boundaries (Fig. 4B). Roughness factor R_f of HT-ALD TiO₂ films ($R_f = 1.10$) is higher compared to LT-ALD TiO₂ films ($R_f = 1.03$). Nanomorphology of as-deposited HT-ALD TiO₂ film (Fig. 4C) did not significantly change after post-annealing (500 °C/1 h) procedure (Fig. 4D).

Dissipation AFM mode based on energy loss during tip-sample interaction is mapping surface nanomechanical properties beyond simple topography and therefore it is used to clarify presence/absence of surface grain-boundary structures independently on the surface roughness (Fig. S4). While surface of annealed LT-ALD TiO₂ (Fig. S4A) is composed from crystalline grains of different orientation with clearly recognized boundaries, the surface of annealed HT-ALD TiO₂ (Fig. S4B) shows no such grain-boundary nanomorphology.

Electrochemical barrier properties of ALD films deposited on FTO

Redox system $[\text{Fe}(\text{CN})_6]^{3-/4-}$ was used for testing the electrochemical blocking properties of ALD TiO₂/FTO films. The

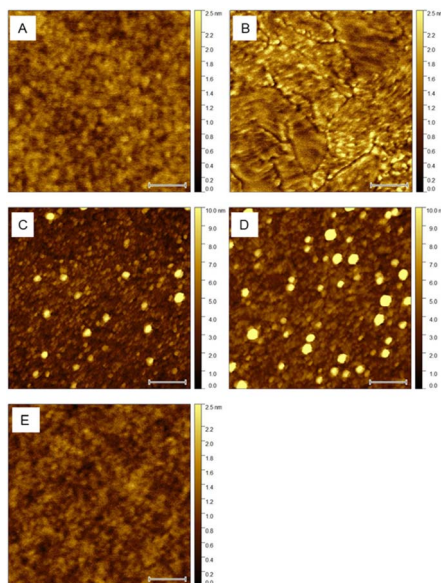


Fig. 4 AFM height images (0.5 μm × 0.5 μm) of 8 nm TiO₂ layers on SiO₂/Si support – as deposited (A and C) and annealed (B and D). (A) As deposited LT-ALD TiO₂, $R_f = 1.03$; (B) annealed LT-ALD TiO₂, $R_f = 1.03$; (C) as deposited HT-ALD TiO₂, $R_f = 1.10$; (D) annealed HT-ALD TiO₂, $R_f = 1.10$; (E) bare SiO₂/Si $R_f = 1.02$. White bars represent 100 nm.

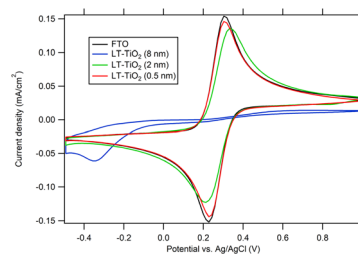


Fig. 5 CVs of 0.5 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ and 0.5 mM $\text{K}_4[\text{Fe}(\text{CN})_6]$ in 0.5 M KCl on FTO electrodes covered with as-deposited LT-ALD TiO₂ films with thickness values of 0.5, 2 and 8 nm, respectively. The scan rate was 50 mV s^{-1} .

$[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple was chosen as a simple one-electron transfer-reaction probe with redox potential positive to flatband of TiO₂. Thus titanium dioxide behaves like an electrochemically silent dielectric material against the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ couple and the charge-transfer reaction is assumed to occur solely at FTO surface directly exposed to the electrolyte solution.²⁷ While the blocking of the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox reaction (decrease in the peak height) was observed for 8 nm LT-ALD TiO₂, for 0.5 and 2 nm thick LT-ALD TiO₂ films the oxidation peak of $[\text{Fe}(\text{CN})_6]^{4-}$ was the same as for bare FTO. The TiO₂ layers were too thin and their barrier properties were not sufficient (Fig. 5).

For the evaluation of the FTO surface fraction covered by the titania blocking layer the method described previously by Kavan *et al.*²⁷ was used. The effective pinhole area (EPA_{EC}) can be expressed by the eqn (1).

$$\text{EPA}_{\text{EC}} = A_{\text{uc}}/A_0 = j_{\text{p}}/j_{\text{p,FTO}} \times 100 (\%) \quad (1)$$

where A_{uc} is the uncovered area of FTO and $j_{\text{p,FTO}}$ is the peak current density measured at a bare FTO electrode; j_{p} is the peak current density measured at the TiO₂/FTO electrode and A_0 is projected electrode area. The blocking characteristics (EPA_{EC}) are summarized in Table 1.

As suggested in work²⁷ there are two types of defects in the barrier film: The “defect A”, in which the partially blocked electrode behaves like “clean” FTO, but with a relatively smaller effective area. The relative increase of the voltammetric peak separation $\Delta E_{\text{pp}} < 3$ (ΔE_{pp} is defined as the difference between the peak potential values for the $\text{Fe}(\text{CN})_6^{4-}$ oxidation and $\text{Fe}(\text{CN})_6^{3-}$ reduction on the blocking layer, normalized to that on pure FTO). The “defect B” is a more complex situation, in

Table 1 The blocking properties ALD TiO₂ layers on FTO

	As deposited		Annealed	
	$\text{EPA}_{\text{EC}}/\%$	Defect type	$\text{EPA}_{\text{EC}}/\%$	Defect type
8 nm LT-TiO ₂	7	B	43	A/B
20 nm LT-TiO ₂	6	B	18	B
50 nm LT-TiO ₂	1	B	2	B
8 nm HT-TiO ₂	—	—	17	A/B
20 nm HT-TiO ₂	—	—	5	B
50 nm HT-TiO ₂	—	—	1	B



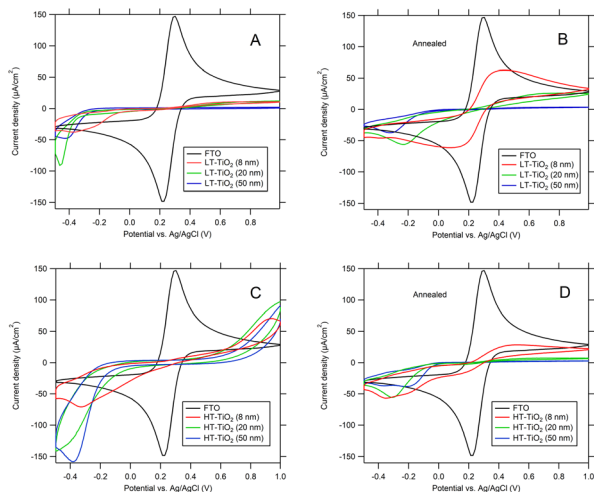


Fig. 6 Influence of film thickness on the blocking properties of ALD-TiO₂ films as-deposited (A and C), and after annealing (500 °C/1 h) (B and D). LT – ALD TiO₂ (A and B); HT – ALD TiO₂ (C and D); electrolyte 0.5 mM K₃[Fe(CN)₆] and 0.5 mM K₄[Fe(CN)₆] in 0.5 M KCl. The scan rate was 50 mV s⁻¹.

which the defect not only causes the delamination of the titanium dioxide film from the FTO substrate, but also the slow-down of charge transfer kinetics (accompanied by a strong increase in ΔE_{pp}).

Blocking properties of as-deposited ALD TiO₂ layers and after annealing (layer thickness 8 nm, 20 nm and 50 nm) are shown in Fig. 6. As-deposited LT-ALD TiO₂ layers of thickness 8–50 nm FTO blocked well electrochemical reaction of [Fe(CN)₆]^{3-/4-} (Fig. 6A), increasing thickness decrease the calculated value of EPA_{EC}. The annealing decreased its barrier properties (Fig. 6B) due to rearrangement of TiO₂ to crystalline nanograins (Fig. 4B and S4A), which boundaries may allow leakage of electrolyte to FTO support. Then, FTO support covered by TiO₂ film may acts as array of microelectrodes, where spherical diffusion may affect the shape of voltammetric curves (Fig. 6). Still, the large (>>59 mV) potential separation of anodic and cathodic redox current maxima and pronounced peak shoulders indicate also slow kinetics with iR drop contribution, which both affect the EPA_{EC} estimation with an error rising with thickness of TiO₂ deposit blocking layer.

In the case of as-deposited HT-ALD TiO₂, we cannot distinguish between redox reaction taking place at conductive FTO

and self-doped HT-ALD TiO₂ (Fig. 6C), thus the determination of pinhole area by this method is not applicable. An alternative electrochemical barrier evaluation can be performed using the electrochemical reaction of a substrate other than bare FTO that has a specific electrochemical response, for example, an Au substrate. However, a disadvantage of this technique—besides the high cost of Au substrates—is the relatively high mobility of Au, which can alter the performance of ALD films, especially after annealing, due to Au contamination.^{28,29}

After re-oxidation of self-doped HT-TiO₂ layer by annealing, the determination of its electrochemical blocking properties become feasible (Fig. 6D). Nevertheless, the cyclic voltammetry yields peaks with shoulders, less pronounced current maxima, and large peak separation, which indicate only slow reaction kinetics, because absence of grain boundaries (Fig. S4B) excluded microelectrode effect.

Chemical stability

Chemical stability of TiO₂ films deposited on FTO support in 0.1 M HClO₄ (pH 1) and 0.1 M phosphate buffer (pH 8) was evaluated from dissolution rates in these solutions (Table 2). The samples were exposed to different electrolytes for 72 hours in dark. The dissolution rates (nm h⁻¹) of TiO₂ were calculated from concentrations of titanium dissolved in electrolytes determined by ICP analysis, using the geometric area of exposed TiO₂ films (2 cm²), the volume of the electrolyte (20 ml) and the density of TiO₂ ($\rho_{\text{amorphous}} = 3.59 \text{ g cm}^{-3}$ for as-deposited TiO₂ films and annealed HT-ALD TiO₂, $\rho_{\text{anatase}} = 3.77 \text{ g cm}^{-3}$ for annealed LT-ALD TiO₂ (ref. 16)) neglecting porosity of the films and assuming uniform coverage (Table 2). In acidic solution more than 40% LT-ALD and 60% HT-ALD of TiO₂ thickness (z) was dissolved after 72 h exposure. Post annealing (500 °C/1 h) caused mild improvement of chemical stability for both LT-ALD and HT-ALD TiO₂.

The etching of both as-deposited and annealed LT-ALD TiO₂ films by exposing to acidic solution led to the formation of pinholes with submicron area and depth $7.6 \pm 0.3 \text{ nm}$ determined from AFM profile analysis of all pinholes appearing in examined areas (Fig. 7A, B and S5A–S5B). This value corresponds to the thickness ($\approx 8 \text{ nm}$) of deposited TiO₂. Surface nanomorphology after etching (Fig. 7C and S5C in SI) was identical (except pinholes) to the nanomorphology of original LT-ALD TiO₂ film (Fig. 4).

Table 2 Dissolution rates of 8 nm TiO₂ films determined by ICP-OES analysis^a

Sample	Solution	z/nm	Dissolution rate/nm h ⁻¹
As dep. LT- TiO ₂	0.1 M HClO ₄	3.83 ± 0.38	0.053 ± 0.005
Anneal. LT-TiO ₂		2.69 ± 0.20	0.038 ± 0.003
As dep LT- TiO ₂	0.1 M PB (pH 8)	0.28 ± 0.03	0.004 ± 0.001
Anneal. LT-TiO ₂		0	0
As dep. HT- TiO ₂	0.1 M HClO ₄	5.25 ± 0.57	0.073 ± 0.008
Anneal. HT-TiO ₂		4.44 ± 0.04	0.061 ± 0.001
As dep. HT- TiO ₂	0.1 M PB (pH 8)	0.61 ± 0.11	0.009 ± 0.002
Anneal. HT-TiO ₂		0	0

^a z concentration of dissolved titanium recalculated to thickness of dense compact TiO₂ layer; PB phosphate buffer.



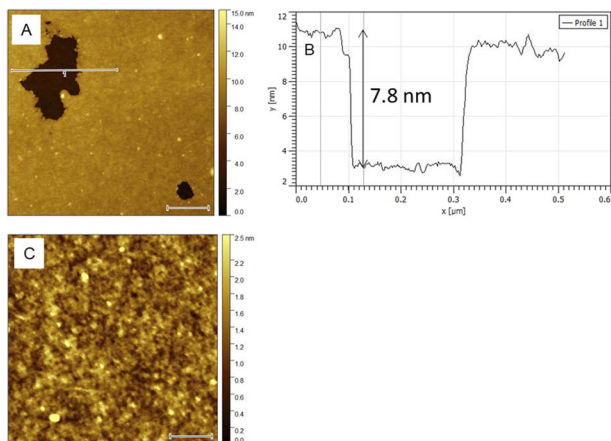


Fig. 7 AFM of as-deposited 8 nm LT-ALD TiO₂ on SiO₂/Si support after 72 h dissolution in 0.1 M HClO₄ pH 1. (A) AFM height image 1 μm × 1 μm, white bar represents 200 nm, line 1 demonstrates pinhole profile analysis (B); (C) AFM height image 0.5 μm × 0.5 μm, surface nanomorphology of TiO₂ outside the pinholes, white bar represents 100 nm.

Based on intact TiO₂ nanomorphology after exposure to acidic media (Fig. 7 and S5 in SI) we can assume, that dissolution occurs only locally, forming pinholes. On this basis, we recalculated the amount of dissolved titanium, determined by ICP-OES analysis, to the area, which would be uniformly covered by dense, 8 nm thick TiO₂ film. This area (A_{ph}), corresponding to sum of areas of all pinholes, was normalized to total surface area ($A_{\text{tot}} = 2 \text{ cm}^2$) of the sample. This ratio (eqn (2)) thus represents relative increase in effective pinhole area after the exposure to acidic media. While EPA_{EC} was determined from electrochemical barrier properties (see Section 3.2), the value obtained from ICP results is denoted as $\Delta\text{EPA}_{\text{ICP}}$ (Eqn (2)). The error of the $\Delta\text{EPA}_{\text{ICP}}$ determination (max. 10%) is governed by the fluctuation of amount of dissolved titania (Table 2).

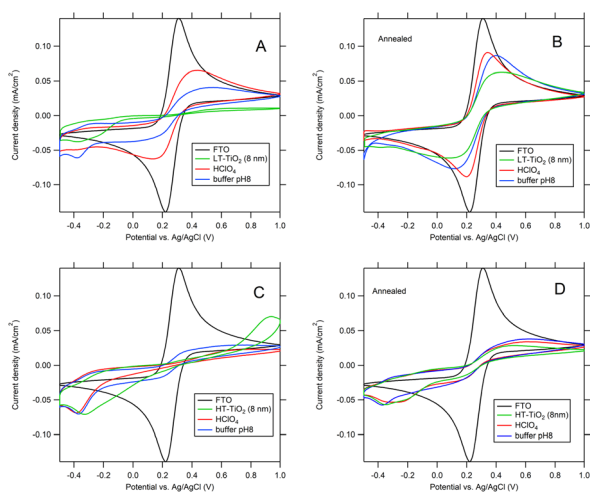


Fig. 8 The blocking properties of 8 nm ALD TiO₂ layers as deposited (A and C) and annealed (B and D) on FTO after 72 h exposure to 0.1 M HClO₄ pH = 1, and 0.1 M phosphate buffer pH = 8. (A and B) LT-ALD TiO₂; (C and D) HT-ALD TiO₂. The scan rate was 50 mV s⁻¹.

$$\Delta\text{EPA}_{\text{ICP}} = A_{\text{ph}}/A_{\text{tot}} \times 100 (\%) \quad (2)$$

Fig. 8 shows, that electrochemical blocking properties of 8 nm TiO₂/FTO electrodes after 72 h exposure to different solution (pH 1 and 8) decreased for all studied TiO₂ layers. The shape of voltammetric curves (red curves in Fig. 8A and B) of electrode with pinholes etched in TiO₂ layer indicates slower kinetics rather than involvement of microelectrode effect.

Difference of EPA evaluated from current peak density of redox reaction of ferro/ferricyanide on TiO₂/FTO electrodes before and after dissolution experiment (Table S2) is denoted as $\Delta\text{EPA}_{\text{EC}}$. Table 3 correlates values of $\Delta\text{EPA}_{\text{ICP}}$ with $\Delta\text{EPA}_{\text{EC}}$. While both methods show good agreement for LT-ALD TiO₂ exposed to an acidic environment, determining of chemical stability in an alkaline environment is likely more complicated. Although the ICP-OES analysis indicated the dissolution of less than 4% of LT-ALD TiO₂ (Table 2), its electrochemical blocking properties after 72 h exposure to phosphate buffer (pH 8) significantly decreased (Fig. 8A, B and Table 3). This discrepancy can be explained by adsorption of phosphate on TiO₂,^{30,31} and formation of several types of Ti-phosphate complexes such as Ti(OH)(H₂PO₄)·2H₂O and *etc.*,³¹ which decreased amount of dissolved titanium in solution available for ICP-OES analysis and influenced electrochemical blocking properties of TiO₂ layer. Presence of ~2 nm thick layer on annealed LT-ALD TiO₂ observed by AFM (Fig. 9A and B) after exposition to phosphate buffer (pH 8), appears to confirm formation of adsorbed layer on TiO₂ surface. No pinholes were observed in examined areas after exposure to phosphate buffer pH 8.

In the case of as-deposited HT-ALD TiO₂, mentioned above, determination of barrier properties using electrochemical

Table 3 A relative increase in effective pinhole area (EPA) in 8 nm TiO₂ film after 72 h dissolution in 0.1 M HClO₄ pH = 1 and 0.1 M phosphate buffer pH = 8, calculated from chemical (ICP) and electrochemical analysis (EC)

Sample	$\Delta\text{EPA}_{\text{ICP}}$ (%)		$\Delta\text{EPA}_{\text{EC}}$ (%)	
	pH 1	pH 8	pH 1	pH 8
LT-ALD TiO ₂	48	40	22	22
LT-ALD TiO ₂ annealed	34	22	22	19
HT-ALD TiO ₂	65	—	—	—
HT-ALD TiO ₂ annealed	56	7	7	10

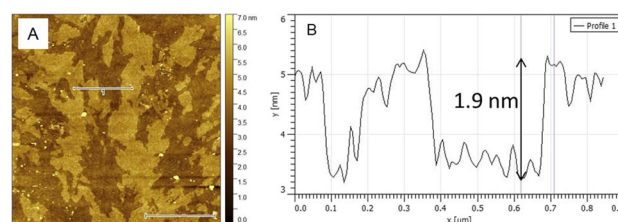


Fig. 9 AFM of annealed 8 nm LT-ALD TiO₂ on SiO₂/Si support after 72 h dissolution in 0.1 M phosphate buffer pH 8. (A) AFM height image (white bar represents 1 μm), line 1 shows location of profile analysis (B).



model redox couple cannot be used due to presence of self-doped sites. For annealed HT-ALD TiO₂, the XPS analysis did not detect presence of low valence titanium (the concentration of Ti³⁺ may be below the detection limit of XPS, which is only 0.5 at%),³² but the large differences between the ΔEPA_{ICP} and values ΔEPA_{EC} (Table 3), together with the yellowish color of annealed HT-ALD TiO₂ films (Fig. 2D), typical for nonstoichiometric TiO₂,²⁵ indicate, that the electrochemical method of determination pinholes area has limited validity also for annealed HT-ALD TiO₂ electrodes.

Long-term stability (168 h) was tested for 8 nm as-deposited LT-ALD TiO₂/FTO. Fig. S6 (in SI) shows the electrochemical blocking properties of LT-TiO₂/FTO electrode after dissolution in 1 M NaOH, 1 M H₂SO₄ and neutral phosphate buffer. After 168 hours exposure to sulphuric acid 8 nm LT-ALD TiO₂ was totally decomposed, effective pinhole area reached 99%, while exposure to solutions of neutral and alkaline pH led to EPA increase to 13% and 27% respectively (Fig. S6 in SI).

Photoelectrochemistry

Fig. 10 shows the incident photon to current conversion efficiency (IPCE) spectra for both types of ALD films measured at applied potential 1 V vs. Ag/AgCl. Fig. S7 then shows photocurrent for irradiation at 369 nm (where IPCE values are very small) as a function of time. As-deposited HT-ALD TiO₂ films exhibit significantly higher (4 times) IPCE values compared to as-deposited LT-ALD TiO₂, which can be explained by the self-doping.^{25,33,34} For as-deposited HT-ALD TiO₂ the presence of low valence titanium introduce electronic states within the bandgap of TiO₂ and caused the shift of absorption edge to longer wavelength.³³ Several recent studies have shown that amorphous or disordered materials can display higher photocatalytic activity than their crystalline counterparts. *E.g.* Zywitzki³⁵ reports amorphous TiO₂ with Ti³⁺ which has blue color and is active in photocatalytic H₂ generation. Enhancement of photoactivity due to the presence of Ti³⁺ but in crystalline TiO₂ was also reported.^{36–38}

Annealing of LT-ALD TiO₂ films caused significant (4–5 times) increase of IPCE, this can be explained by the formation of anatase crystalline structure. An increase in the photocurrent at 369 nm is even higher (20–40 times). Annealing of HT-ALD

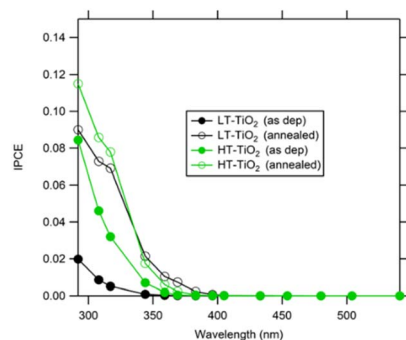


Fig. 10 IPCE spectra of 8 nm TiO₂/FTO, electrolyte 0.1 M Na₂SO₄, pH 10, potential 1 V vs. Ag/AgCl, illumination geometry EE. LT-ALD TiO₂ – black circles; HT-ALD TiO₂ – green circles. Filled circles – as-deposited TiO₂; open circles – annealed TiO₂.

TiO₂ films results also in an increase in IPCE but in much smaller extent (about 2 times), similar increase was observed for photocurrent at 369 nm. The observed increase in photoelectrochemical response for HT-ALD TiO₂ films is in contradiction with findings that after annealing in air films remain amorphous (Fig. 1D) and according XPS low valent Ti disappears (Fig. 3B). This can be explained by the two facts. First, low valence Ti are present but below the detection limit of XPS analysis. The presence of small amount of low valence Ti is in agreement with the remaining yellowish color of the HT-ALD film after annealing (see Fig. 2D). Similar observation was reported by Wierzbicka *et al.*³⁷ where even small amount of Ti³⁺, not detected by XPS strongly influenced photocatalytic hydrogen evolution. Second, even XRD did not show any crystalline phase, Raman analysis (Fig. S8 in SI) shows the formation of small amount of rutile.

The band gap energy (E_g) was determined from the electrochemical Tauc plot (Fig. S9 in SI). The Tauc – function (indirect transition) was taken as $(\ln(1/(1-IPCE))) \times (h\nu)^{1/2}$.³⁹ The calculated value of E_g is 3.4 and 3.35 eV for as-deposited LT-ALD TiO₂ and HT-ALD TiO₂, respectively. After annealing, the band gap of LT-ALD TiO₂ decreased to 3.1 eV due to the formation of anatase crystalline structure. But for annealed HT-ALD TiO₂ electrodes band gap did not significantly change, which is in agreement with the observed predominant amorphous structure.

Conclusions

Parameters of ALD deposition procedure significantly influence properties of deposited TiO₂ thin films. As-grown TiO₂ films prepared by ALD with deposition temperature 150 °C (LT-ALD) were amorphous, subsequent annealing at 500 °C/1 h led to the formation of anatase crystalline structure indicated by XRD and also manifested by nanomorphology rearrangement. Formation of crystalline nanodomains with visible boundaries was confirmed by AFM. ALD with deposition temperature 250 °C (HT-ALD) forms amorphous non-stoichiometric TiO_{2-x} with presence of low valence titanium. Annealing at 500 °C/1 h in air caused the decrease in the level of doping, but no crystalline structure was detected.

As-deposited LT-ALD TiO₂ layers of thickness 8–50 nm blocked well electrochemical reaction of model redox couple [Fe(CN)₆]^{3-/4-}, calculated EPA was low, but for determination of barrier properties of HT-ALD TiO₂, this method is not applicable, due to presence of self-doped sites.

ALD TiO₂ thin films were unstable in acidic solution, exposure to 0.1 M HClO₄ for 72 h led to the formation of pinholes in TiO₂ film with submicron area and depth corresponding to TiO₂ thickness and dissolution of ~50% and 40% of TiO₂ of as-deposited HT-ALD TiO₂ and LT-ALD TiO₂, respectively. While all tested ALD TiO₂ films showed good chemical stability in alkaline phosphate buffer (pH 8), AFM indicated formation of thin layer on TiO₂ surface, which may influence (photo) electrochemical properties of TiO₂ electrodes. Photoelectrochemical (PEC) response of as deposited LT-ALD TiO₂/FTO electrode is negligible and significantly increases (about 1



order) due to formation of anatase structure after annealing. Higher PEC response of as deposited HT-ALD TiO₂/FTO electrode compared to as-deposited LT-ALD TiO₂/FTO is caused by Ti³⁺ self-doping. PEC response after annealing of HT-ALD TiO₂/FTO increased even the amount of Ti³⁺ decreased and XRD did not confirm any crystalline phase. This could be explained by the presence of traces of low valent Ti and/or by the formation of small amount of rutile.

Author contributions

Hana Krýsová: layer deposition, electrochemical characterization, reviewing and editing, Tomáš Imrich: investigation, XRD analysis, chemical stability, Hana Tarábková: AFM analysis, writing – original draft preparation, reviewing and editing, Pavel Janda: AFM analysis, reviewing and editing, Josef Krýsa: conceptualization, writing, reviewing and editing.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data presented in this study are available at <https://doi.org/10.5281/zenodo.17829888>. Data set for “Impact of variations in ALD procedure on nanomorphology, protecting properties and chemical stability of thin TiO₂ Films” (Original data) (Zenodo).

Supplementary information (SI) is available. See DOI: <https://doi.org/10.1039/d5ra09703g>.

Acknowledgements

This work was supported by the Czech Science Foundation (Project No. 23-05266S). This work was also supported by the project “Sensors and Detectors for Future Information Society – SENDISO reg.n. CZ.02.01.01/00/22_008/0004596” by the Programme Johannes Amos Comenius, call “Excellent Research”. The authors also acknowledge the assistance provided by the Research Infrastructure NanoEnviCz, supported by MEYS CR under Project No. LM2023066 and project Pro-NanoEnviCz (Reg. No. CZ.02.1.01/0.0/0.0/16_013/0001821) supported by MEYS CR and EU – European Structural and Investments Funds. M. Kudrnová (University of Chemistry and Technology, Prague) is acknowledged for performing the XPS analysis. B. Pitňa-Lásková (J. Heyrovský Institute of Physical Chemistry, Prague) is acknowledged for performing the Raman spectroscopy analysis.

References

- V. Benavente Llorente, K. J. Jenewein, M. Bierling, A. Körner, A. Hutzler, A. Kormányos and S. Cherevko, *J. Phys. Chem. C*, 2023, **127**, 19687–19697.
- D. Dworschak, C. Brunnhofer and M. Valtiner, *ACS Appl. Mater. Interfaces*, 2020, **12**, 51530–51536.
- J. Knöppel, A. Kormányos, B. Mayerhöfer, A. Hofer, M. Bierling, J. Bachmann, S. Thiele and S. Cherevko, *ACS Phys. Chem. Au*, 2021, **1**, 6–13.
- B. Weng, M. Y. Qi, C. Han, Z. R. Tang and Y. J. Xu, *ACS Catal.*, 2019, **9**, 4642–4687.
- S. M. George, *Chem. Rev.*, 2010, **110**, 111–131.
- T. Imrich, M. Neumann-Spallart, H. Krýsová, H. Tarábková, R. Nebel and J. Krýsa, *J. Photochem. Photobiol. A Chem.*, 2023, **445**, 115026.
- T. Imrich, H. Krýsová, M. Neumann-Spallart and J. Krýsa, *J. Electroanal. Chem.*, 2021, **892**, 115282.
- T. Imrich, R. Zazpe, H. Krýsová, Š. Paušová, F. Dvorak, J. Rodriguez-Pereira, J. Michalicka, O. Man, J. M. Macak, M. Neumann-Spallart and J. Krýsa, *J. Photochem. Photobiol. A Chem.*, 2021, **409**, 113126.
- T. Moehl, J. Suh, L. Sévery, R. Wick-Joliat and S. D. Tilley, *ACS Appl. Mater. Interfaces*, 2017, **9**, 43614–43622.
- B. O'Regan and M. Grätzel, *Nature*, 1991, **353**, 737–740.
- T.-C. Wu, W.-M. Huang, J.-K. Tsai, C.-E. Chang and T.-H. Meen, *Coatings*, 2024, **14**, 304.
- H. Krýsová, M. Neumann-Spallart, H. Tarábková, P. Janda, L. Kavan and J. Krýsa, *Beilstein J. Nanotechnol.*, 2021, **12**, 24–34.
- K. Wang, A. Paxson, T. I. Valdez, A. G. Erlat, P. C. Lee, S. Yun, A. C. Kummel and P. R. Bandaru, *Appl. Surf. Sci.*, 2025, **692**, 162719.
- Q. Xie, Y.-L. Jiang, C. Detavernier, D. Deduytsche, R. L. Van Meirhaeghe, G.-P. Ru, B.-Z. Li and X.-P. Qu, *J. Appl. Phys.*, 2007, **102**, 083521.
- S. Kim, R. Hidayat, H. Roh, J. Kim, H. L. Kim, K. Khumaini, M. Park, J. H. Seok, J. W. Park and W. J. Lee, *J. Mater. Chem. C*, 2022, **10**, 6696–6709.
- W. Chiappim, G. E. Testoni, R. S. Moraes, R. S. Pessoa, J. C. Sagas, F. D. Origo, H. S. Maciel and L. Vieira, *Vacuum*, 2016, **123**, 91–102.
- J.-P. Niemelä, G. Marin and M. Karppinen, *Semicond. Sci. Technol.*, 2017, **32**, 093005.
- B. Abendroth, T. Moebus, S. Rentrop, R. Strohmeyer, M. Vinnichenko, T. Weling, H. Stöcker and D. C. Meyer, *Thin Solid Films*, 2013, **545**, 176–182.
- J. P. Wooding, S. A. Gregory, A. Atassi, G. Freychet, K. Kalaitzidou and M. D. Losego, *At. Layer Deposition*, 2023, **1**, 1–18.
- M. Zlamalova, V. Mansfeldova, H. Tarabkova, H. Krysova and L. Kavan, *J. Solid State Electrochem.*, 2023, **27**, 1935–1943.
- Q. Xie, J. Musschoot, D. Deduytsche, R. L. Van Meirhaeghe, C. Detavernier, S. Van den Berghe, Y.-L. Jiang, G.-P. Ru, B.-Z. Li and X.-P. Qu, *J. Electrochem. Soc.*, 2008, **155**, H688.
- Powder Diffraction File Alphabetic PDF-4 Data Base, *International Center of Diffraction Data*, Newtown Square, PA, USA, 2023.
- E. Temur, M. Eryigit, H. Öztürk Doğan, E. Çepni and Ü. Demir, *Appl. Surf. Sci.*, 2022, **581**, 152150.
- S. Wang, J. Cai, J. Mao, S. Li, J. Shen, S. Gao, J. Huang, X. Wang, I. P. Parkin and Y. Lai, *Appl. Surf. Sci.*, 2019, **467–468**, 45–55.



- 25 X. Pan, M. Q. Yang, X. Fu, N. Zhang and Y. J. Xu, *Nanoscale*, 2013, **5**, 3601–3614.
- 26 J. Saari, H. Ali-Löytty, M. M. Kauppinen, M. Hannula, R. Khan, K. Lahtonen, L. Palmolahti, A. Tukiainen, H. Grönbeck, N. V. Tkachenko and M. Valden, *J. Phys. Chem. C*, 2022, **126**, 4542–4554.
- 27 L. Kavan, N. Tétreault, T. Moehl and M. Grätzel, *J. Phys. Chem. C*, 2014, **118**, 16408–16418.
- 28 C. A. Ihalawela, M. Sundararajan, K. W. Cooper, M. E. Kordesch, D. C. Ingram, X.-M. Lin and G. Chen, *Phys. Status Solidi*, 2021, **258**, 1–5.
- 29 N. Milićević, M. Novaković, J. Potočnik, M. Milović, L. Rakočević, N. Abazović and D. Pjević, *Surf. Interfaces*, 2022, **30**, 101811.
- 30 R. A. Mathew, G. Wu, Y. Zhang, S. Shakiba, Y. Yao, A. L. Tsai and S. M. Louie, *Environ. Sci. Nano*, 2021, **8**, 2165–2176.
- 31 S. A. Kang, W. Li, H. E. Lee, B. L. Phillips and Y. J. Lee, *J. Colloid Interface Sci.*, 2011, **364**, 455–461.
- 32 Z. Zhang, S. D. Qin, J. Y. Chen, J. Li and A. H. Xing, *J. Chem. Res.*, 2021, **45**, 443–449.
- 33 H. Pelouchova, P. Janda, J. Weber and L. Kavan, *J. Electroanal. Chem.*, 2004, **566**, 73–83.
- 34 N. S. Portillo-Vélez, O. Olvera-Neria, I. Hernández-Pérez and A. Rubio-Ponce, *Surf. Sci.*, 2013, **616**, 115–119.
- 35 D. Zywitzki, H. Jing, H. Tüysüz and C. K. Chan, *J. Mater. Chem. A*, 2017, **5**, 10957–10967.
- 36 X. Liu, G. Du and M. Li, *ACS Omega*, 2019, **4**, 14902–14912.
- 37 E. Wierzbicka, B. Osuagwu, N. Denisov, D. Fehn, K. Meyer and P. Schmuki, *IOP Conf. Ser. Mater. Sci. Eng.*, 2020, **908**, 6–11.
- 38 J. Kuang, Z. Xing, J. Yin, Z. Li, S. Tan, M. Li, J. Jiang, Q. Zhu and W. Zhou, *Arab. J. Chem.*, 2020, **13**, 2568–2578.
- 39 T. Imrich, H. Krýsová, M. Neumann-Spallart and J. Krýsa, *Catal. Today*, 2023, **413–415**, 113982.

