Atomic Layer Deposition Al$_2$O$_3$ Coatings Significantly Improve Thermal, Chemical, and Mechanical Stability of Anodic TiO$_2$ Nanotube Layers

Raul Zazpe,† Jan Prikryl,† Viera Gartnerova,‡ Katerina Nechvilova,§ Ludvik Benes,⊥ Lukas Strizik,†∥ Ales Jäger,‡ Markus Bosund,§ Hanna Sopha,† and Jan M. Macak*†

†Center of Materials and Nanotechnologies, Faculty of Chemical Technology, University of Pardubice, nam. Cs. legii 565, 53002 Pardubice, Czech Republic
‡Laboratory of Nanostructures and Nanomaterials, Institute of Physics of the CAS, v.v.i., Na Slovance 2, 182 21 Prague 8, Czech Republic
§Institute of Chemistry and Technology of Macromolecular Materials, Faculty of Chemical Technology, and ||Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentska 573, 532 10 Pardubice, Czech Republic
⊥Joint laboratory of Solid-State Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentska 95, 532 10 Pardubice, Czech Republic
§Beneq, Olarimluoma 9, 02201 Espoo, Finland

ABSTRACT: We report on a very significant enhancement of the thermal, chemical, and mechanical stability of self-organized TiO$_2$ nanotube layers, provided by thin Al$_2$O$_3$ coatings of different thicknesses prepared by atomic layer deposition (ALD). TiO$_2$ nanotube layers coated with Al$_2$O$_3$ coatings exhibit significantly improved thermal stability as illustrated by the preservation of the nanotubular structure upon annealing treatment at high temperatures (870 °C). In addition, a high anatase content is preserved in the nanotube layers against expectation of the total rutile conversion at such a high temperature. Hardness of the resulting nanotube layers is investigated by nanoindentation measurements and shows strongly improved values compared to uncoated counterparts. Finally, it is demonstrated that Al$_2$O$_3$ coatings guarantee unprecedented chemical stability of TiO$_2$ nanotube layers in harsh environments of concentrated H$_3$PO$_4$ solutions.

INTRODUCTION

Self-organized TiO$_2$ nanotube layers have attracted remarkable attention within the past 15 years due to their unique architecture, high surface area, semiconductive properties, and biocompatibility.1,2 In addition, they are produced by a low-cost electrochemical anodization of Ti substrates in suitable electrolytes containing fluorides. All these features enabled utilization of TiO$_2$ nanotube layers in a wide number of applications as photocatalyst,3,4 anode of dye-sensitized solar cells (DSSC),5,6 and perovskite solar cells (PSC),7,8 gas sensors,9 and biomedical materials,10,11 among others. In all these applications, TiO$_2$ nanotube layers have shown superior performance compared to other TiO$_2$ nanostructures. In parallel, important efforts have been carried out to tune the nanotube aspect ratio12–14 and to improve the nanotube ordering15–17 and crystallinity.18–20 Annealing treatment of amorphous as-synthesized TiO$_2$ nanotube layers leads to their crystallization into anatase (>280 °C), a combination of anatase and rutile (>450 °C), or rutile (>550 °C).18–20

The anatase nanotubular structure has shown to be more favorable than rutile for photoelectrochemically assisted applications, such as photocatalysis3,4 and DSSC.21,22 Thus, the stability of anatase nanotubular structure is highly desired, and numerous efforts have been focused on this target, especially at high temperatures. The introduction of alloying elements as Nb23 or C24 was reported to induce a shift of the anatase to rutile transition (further noted as ART) to higher temperature and increased thermal resistance against collapse. However, the main disadvantage of alloying is the formation of undesired secondary impurity phases, e.g., Ti–Nb$_2$O$_5$.25 The ART threshold depends on whether the nanotube layers are attached or separated from the Ti substrate. High temperature stability (up to 700 °C) of TiO$_2$ nanotube arrays, preserving the nanotubular integrity and anatase structure, was reported for free-standing TiO$_2$ nanotube arrays.26 For TiO$_2$ nanotube
layers attached to Ti substrate, anatase structure and no structural collapse were reported up to 800 °C. The stability against collapse at this temperature is maintained either by a previous solvothermal treatment or previous annealing at lower temperature. The highest published temperature without nanotube collapse (≈1048 °C) was reached during the flame annealing process. However, such flame high temperature processing led to undesired transition to rutile structure and a significant uptake of carbon from the flame. Despite numerous efforts focused onto the high temperature stability of TiO2 nanotube layers, the temperature working window is still restricted. Another constrain for applications of TiO2 nanotube layers is their limited chemical stability in harsh acidic environments, where nanotube layers undergo chemical dissolution.

The improvement of the thermal, chemical, and eventually also mechanical properties of TiO2 nanotube layers would enable their utilization in previously nonimaginable working environments and surely interesting expansion of their application range. In principle, addition of a thin continuous coating of an appropriate secondary material (with excellent thermal and chemical stability) within nanotubes should significantly alter also their stabilities. So far, however, no such treatment has been shown. To date, the atomic layer deposition (ALD) technique is the only method that enables homogeneous, continuous, and conformal coating of secondary materials into TiO2 nanotube layers. Deposition of Al2O3 and ZnO coating by ALD into TiO2 nanotube layers has been reported yielding interesting synergic effects. The resulting composite heterostructures revealed significant improvement of their photovoltaic and photocatalytic performance due to enhanced charge separation induced by coatings of secondary materials.

Therefore, in the present work we investigated the thermal, chemical, and mechanical properties of self-organized TiO2 nanotube layers uniformly coated with Al2O3 layers of different nominal thicknesses: 1, 10, and 42 nm. These coatings were carried out by atomic layer deposition (ALD) using different number of identical deposition cycles. After the Al2O3 coating, the TiO2 nanotube layers were annealed at temperature up to 870 °C for 1 h to evaluate their thermal stability. The resulting crystal structure and composition were analyzed through X-ray diffraction (XRD) and scanning transmission electron microscopy (STEM). Mechanical properties (hardness) were characterized by nanoindentation measurements using an atomic force microscope. The chemical stability was tested by soaking the Al2O3-coated TiO2 nanotube layers into H3PO4 solutions of different concentrations for 48 h at laboratory temperature and for an additional 8 h in solutions with temperature of 60 °C.

**EXPERIMENTAL SECTION**

Self-organized TiO2 nanotube layers with a thickness of ≈20 μm and a nanotube diameter of ≈110 nm (aspect ratio ≈180) were fabricated via anodization of Ti foils using a previously published approach. Prior to anodization, the Ti foils (Sigma-Aldrich, 0.127 mm thick, 99.7% purity) were degreased by sonication in isopropanol and acetone, then rinsed with isopropanol, and dried in air. The electrochemical setup consisted of a two-electrode configuration using a platinum foil as the counter electrode, while Ti foils (working electrodes) were pressed against an O-ring of the electrochemical cell, leaving 1 cm² open to the electrolyte. A high-voltage potentiostat (PGU-200 V, IPS Elektroniklabor GmbH) was employed to carry out the electrochemical experiments at room temperature. Ethylene glycol containing 1.5 vol % deionized water and 176 mM NH4F was used as electrolyte. All electrolytes were prepared from reagent grade chemicals (Sigma-Aldrich). Electrolytes were aged before the first use for 15 h by anodization of blank Ti foils at 60 V under the same conditions for the anodization experiments—reasons for aging were described in the previous literature. Ti foils were anodized for 4 h after sweeping the potential from 0 to 60 V with a sweeping rate of 1 V/s. After anodization the Ti foils were rinsed and sonicated in isopropanol and dried.

The TiO2 nanotube layers by were coated with Al2O3 by atomic layer deposition (ALD) using thermal ALD, TFS 200, Beneq). This technique based on sequential and self-limiting gas—surface reactions allows conformal deposition of various coatings within TiO2 nanotube layers. The growth per cycle value of the Al2O3 process at 200 °C (≈1 A/ cycle). The thicknesses of Al2O3 coatings were confirmed by variable angle spectroscopic ellipsometry (VASE ellipsometer, J.A. Woollam, Co., Inc.) of Al2O3 coatings on Si wafers.

Upon the Al2O3 coating process, the TiO2 nanotube layers were annealed along with reference uncoated layers. The annealing process was carried out in a muffle oven in an air atmosphere applying a heating rate of 15 °C/min, until the target temperature (870 °C) was reached. The annealing process proceeded at such temperature for 1 h. Afterward, the layers were allowed to naturally cool down.

The morphology of the TiO2 nanotube layers was characterized by a field-emission SEM (FE-SEM JEO JSM 7500F) and a scanning transmission electron microscope (STEM, FEI Tecnai F20 X-Twin) fitted with a high angle annular dark field (HAADF) detector and operating at 200 kV. The cross-sectional views were obtained from mechanically bent samples. Because of the rupture of the nanotube layers via this bending, it was possible to visualize nanotubes within the layers and coatings within nanotubes in various directions and nanotube layer depths. Dimensions of the nanotubes were measured and statistically evaluated using proprietary Nanomembre software. Average values and standard deviations were calculated from at least three different locations with a high number of measurements (n > 100).

Diffraction analyses of the Al2O3-coated TiO2 nanotube layers carried out using X-ray diffractometer (XRD, D8 Advance, Bruker AXE) using Cu Kα radiation with secondary graphite monochromator and Na(Tl)F scintillation detector. Nanoindentation measurements were performed to analyze the mechanical properties (hardness) of the TiO2 nanotube layers. They were determined by an atomic force microscope (AFM, SOLVER NEXT, NT MDT) equipped with a nanoindentation head N001NTEF and a Berkovich type of tip (three-sided pyramid geometry with a parameter of static stiffness, k = 10.2 ± 0.3 kN/m). The nanotube layers were measured in longitudinal direction for compressive force of 0.5 mN, loaded for 100 s. Fused silica SiO2 was used as a calibration sample (hardness, H = 9.5 ± 0.5 GPa by ISO 4540-76). The penetration depth of the tip was up to a maximum 10% of the total thickness of the nanotube layer. The hardness was evaluated at ~30 different areas of each nanotube layer to ensure statistically relevant data set/significant results.

The chemical stability of Al2O3-coated TiO2 nanotube layers was analyzed by soaking in H3PO4 solutions of different concentrations: 25, 50, 70, and 85 wt % (prepared from 85 wt % H3PO4, Penta). TiO2 nanotube layers were soaked in these solutions for 48 h, including a thermal treatment for 8 h by which solutions were heated up at 60 °C.
to further study the nanotube chemical stability under warm acidic conditions. Before the subsequent SEM analysis, the layers were rinsed with water and dried in air.

■ RESULTS AND DISCUSSION

Al₂O₃ Coating of TiO₂ Nanotube Layers. Highly ordered TiO₂ nanotube layers, with a thickness of $\approx 20 \mu m$ and an average diameter value of $\approx 110$ nm (aspect ratio $\approx 180$), were prepared by anodization of Ti foils as described in detail in the Experimental Section. As-prepared amorphous TiO₂ nanotube layers were coated with Al₂O₃ of different nominal thicknesses, namely 1, 10, and 42 nm by ALD, as verified by SEM and ellipsometric measurements (1.1 ± 0.2, 10 ± 0.5, and 44 ± 2.1 nm). Freshly coated nanotube layers were annealed at 870 °C for 1 h along with reference uncoated TiO₂ nanotube layers. Figure 1 shows SEM images of the TiO₂ nanotube layers with and without Al₂O₃ coating annealed at 870 °C. Uncoated TiO₂ nanotube layers (Figure 1a) collapsed during the annealing process into a pillar nanostructure (Figure 1b). When coated, the nanotube layers were preserved after the annealing process, regardless of the thickness of the Al₂O₃, as apparent for coatings of either 1 nm (Figure 1c,d), or 10 nm (Figure 1e,f). It is quite fascinating that even 1 nm thin Al₂O₃ coating can build a very thermally robust cage all over TiO₂ nanotubes with some 20–40 nm thick tube walls.

Figure 2 shows representative STEM-HAADF images of the nanotube body (separated from the annealed Al₂O₃ coated (10 nm) TiO₂ nanotube layer by mechanical bending of the layers followed by sonication in methanol) at a low (a) and at a high magnification (b). Especially from Figure 2b, the interface between the TiO₂ wall and Al₂O₃ coating is well distinguishable. There are actually two interfaces between the TiO₂ wall and Al₂O₃ coating, as the Al₂O₃ coating is deposited inside (interior coating) and outside (exterior coating) the TiO₂ tube walls. This feature is in accordance with our previous ALD work, where we showed very good uniformity of Al₂O₃.
coatings on the amorphous tubes and absence of any pinholes in the coating. As apparent from Figure 2, Al2O3 coatings remained continuous and pinhole-free even after annealing, during which thermally induced crystallization of TiO2 tube walls occurred. Some delamination of the coating seen at the outer and inner interface between TiO2 wall and Al2O3 coating (especially at Figure 2b) stems most likely from the stress that these layers are exposed to during the preparation of specimens for SEM and STEM observation, which includes mechanical rupture of layers. These roughening and delamination events have no detrimental effect on coated nanotube layers that were not submitted for SEM and STEM and that completely survived soaking in H3PO4 solutions (described later in text).  

**Influence of the Coating on Crystal Structure.** It is generally accepted that the annealing process influences crystal structure, phase transition, and structural integrity of the TiO2 nanotube layers.18–20 It has also been accepted that amorphous as-prepared TiO2 nanotube layers crystallize into anatase above 280 °C in air.2 The anatase to rutile transition (ART) has been reported at different temperatures, most usually in the range of temperature between 500 and 600 °C, depending on the nanotube dimensions (diameter, thickness, and composition). Annealing at temperatures higher ≥600 °C leads to the coexistence of anatase and rutile structures, while total conversion to rutile structure takes place above 800 °C.2,39

Figure 3a shows the XRD pattern obtained for reference uncoated TiO2 nanotube layers annealed for 1 h at either 400 or 870 °C, respectively. In line with literature, the former exhibits pure anatase crystal phase identified by typical anatase peaks associated with planes (101), (004), (105), and (211), with a dominant orientation (101). The latter reveals pure rutile crystal phase with well-defined diffraction peaks of planes (110), (011), (111), (211), and (220). The intensity of the peak at 2θ = 27.4° indicates a preferred orientation along the (110) direction; no trace of anatase polymorphic phase is detected.

The XRD patterns, obtained from Al2O3-coated TiO2 nanotube layers annealed at 870 °C for 1 h, are shown in Figure 3. The XRD patterns of (a) uncoated TiO2 nanotube layers annealed at 870 and 400 °C for 1 h; (b) Al2O3-coated TiO2 nanotube layers with different coating thicknesses (1, 10, and 42 nm) annealed at 870 °C for 1 h; and (c) Al2O3-coated (1 and 10 nm) TiO2 nanotube layers preannealed (400 °C, 1 h) and second annealing at 870 °C. A = anatase, R = rutile, and T = titanium substrate.

Figure 3b. Therein the coexistence of anatase and rutile structures can be clearly seen, in contrast to the uncoated nanotube layers (Figure 3a) where rutile was exclusively formed at this temperature, in line with the previous work.18 The incomplete ART of coated TiO2 nanotube layers annealed at 870 °C stems from the hindered surface reconstruction of the TiO2 due to Al2O3 coating and also the impact of Al3+ as the phase transformation inhibitor.40 In contrast, for uncoated nanotube layers (annealed at 870 °C) the surface’s reconstruction can easily take place (no space constrains are present), allowing for the mass flow and rearrangements that yield complete rutile conversion, expected at this temperature.18 Another evidence for limited reconstruction of coated TiO2 nanotube layers annealed at 870 °C is the fact that they do not collapse (sinter), which they would otherwise do without coating. In the case of thermally stable coated nanotube layers, the coating acts in similar fashion as it does for nanoparticles and nanorods that can be annealed, when coated, at high temperatures without undergoing sintering events.41,42

Quantification of the content of each crystal phase and an average of the corresponding crystallite size are given in Table 1.

The anatase:rutile ratio was found to be dependent on the Al2O3 coating. The nanotube layer with the thickest Al2O3 coating (42 nm) exhibited dominant rutile structure (62%) with peaks corresponding to the planes (110), (001), (111), (211), and (220) and only one minor anatase peak corresponding to (101) plane. In clear contrast, the anatase content for 10 and 1 nm thin Al2O3 coating was found to increase up to 73% and 83%, respectively, on account of rutile.
There is a clear link between the experimental results obtained in this work and the literature about factors affecting the ART.45,44 According to Figure 3, the anatase:rutile ratio is clearly dependent on the Al2O3 coating thickness. Assuming the results by Rath et al.43 that larger number of oxygen vacancies promotes the ART, it is clear that the Al2O3 coating within our TiO2 nanotube layers influences the number of oxygen vacancies as it possesses a barrier against the oxygen diffusion.50 For example, the thickest Al2O3 coating (42 nm) hinders the oxygen diffusion most significantly from all used coatings in this work, leads to highest number of oxygen vacancies within TiO2 nanotubes, and boosts the ART process that ends up with the highest rutile content. In contrast, the oxygen diffusion into TiO2 takes place more easily through thinner Al2O3 coatings (1 and 10 nm), resulting in a lower number of oxygen vacancies, retarding the ART within TiO2 nanotubes. In addition, the largest rutile crystal size, calculated by the Scherrer equation (Table 1), corresponds to the thickest Al2O3 coating, which also corroborates previously published findings on ART and size of rutile crystals.45,46

To get a complete picture about the ART, we also fully explored anatase TiO2 nanotube layers (annealed at 400 °C for 1 h), shown in Figure 3a, for Al2O3 coating. We coated these nanotube layers with 1 and 10 nm of Al2O3 by ALD, before undergoing a second thermal treatment at 870 °C for 1 h. First, the Figure 3c shows that the Al2O3-coated (10 nm) TiO2 nanotube layer consisted of 100% rutile, while in the Al2O3-coated (1 nm) TiO2 nanotube layer rutile content was only 26%. These results confirm the active role of the Al2O3 coating for TiO2 crystal structure and are in line with the results and theories discussed in Figure 3b. Second, the significantly different crystal structure of the both investigated types of Al2O3 (10 nm) TiO2 nanotube layer were revealed. The formerly annealed Al2O3 coated (10 nm) TiO2 nanotube layer (fully anatase comprised) underwent a complete ART and was 100% rutile comprised (see Figure 3c). In contrast, the initially amorphous TiO2 nanotube layer revealed a predominant anatase content of ≥74% (see Figure 3b). This comparison clearly confirms that the TiO2 structure influences the ART and that it is clearly promoted for the TiO2 nanotube layers annealed to anatase before ART and ALD coating. In other words, the lack of coating induces during the thermal annealing to 400 °C more oxygen vacancies in the TiO2 nanotube layers than it does when coatings are present during this annealing step.

**Mechanical Properties.** The mechanical integrity of the TiO2 nanotube layers is of significant importance, especially for synthesis of devices based on flow-through membranes utilizing nanotube layers opened on both sides.51 Even though some nanoindentation analyses of the TiO2 nanotube arrays were already carried out,52–59 nanotube layers modified with additional coatings, as in the present case, have not yet been analyzed. Figure 4 shows hardness of TiO2 nanotube layers with Al2O3 coatings of different thicknesses as well as two reference nanotube layers. If not denoted otherwise, all nanotube layers were annealed at 870 °C for 1 h as the last processing step. The obtained hardness values show two prominent features. First, the uncoated amorphous (i.e., did not undergo annealing) TiO2 nanotube layer displayed lower hardness value than the annealed uncoated counterpart, fully rutile structure comprised. That was expected as the crystal structure has (as a rule of thumb) higher hardness than amorphous mass of the same compound. Second, the annealed
Al₂O₃-coated TiO₂ nanotube layers exhibited larger hardness with the increasing Al₂O₃ coating thickness. This can be ascribed to increasing content of rutile (Table 1) and to an increasing Al₂O₃ mass within the nanotubes.

Even though rutile and anatase are similar in structure, the reason to rutile to be more mechanically robust than anatase is that its octahedra shares four edges instead four corners (anatase case), which leads to the formation of chains arranged subsequently in a 4-fold arrangement.⁵⁷,⁵⁹ This also explains why the Al₂O₃-coated (1 nm) TiO₂ coated layer (which has mainly anatase structure as shown in Figure 3b) has lower hardness than uncoated annealed layers (completely rutile based, also shown in Figure 3a).

The hardness values presented here for high aspect ratio (≈180) nanotube layers were larger than those found in the literature that reports typical hardness in the range from 94 MPa to ≈3.5 GPa.⁵²,⁵⁴,⁵⁷,⁵⁸ However, it is difficult to establish a

![Graph showing hardness of different TiO₂ nanotube layers determined by nanoindentation measurements. Except for the sample marked “uncoated”, all nanotube layers were annealed at 870 °C for 1 h.](image)

![SEM top-view images of annealed Al₂O₃-coated (1 nm) TiO₂ nanotube layers before (a) and after soaking in H₃PO₄ solutions with different concentrations: (b) 50 wt %, (c) 70 wt %, and (d) 85 wt % in total for 48 h (last 8 h at 60 °C). SEM top-view images of reference uncoated amorphous (e) and anatase (f) TiO₂ nanotube layers after soaking in H₃PO₄ solutions of 10 and 40 wt %, respectively, for 24 h. All the scale bars denote 100 nm.](image)
improved charge separation on the interface with various acidic (H2SO4, HNO3, HCl) and alkaline (KOH) environments.60 To make the H3PO4 environment even more harsh, the H3PO4 solutions were heated up to 60 °C, and soaking was carried out for an additional 8 h (in total 48 h). Since again no visible changes were observed, soaking experiments were terminated afterward. Reference uncoated layers (namely as-anodized amorphous and annealed (400 °C for 1 h) nanotube layers) did not survive these conditions. In order to determine the chemical threshold conditions for these reference uncoated layers, lower H3PO4 concentrations had to be used. The stability threshold was revealed to be 10 wt % (Figure 5e) and 40 wt % (Figure 5f) on the scale of 24 h for the amorphous and annealed case, respectively, without any heating. All in all, the results presented in Figure 5 for Al2O3-coated nanotube layers confirm the outstanding enhancement of the chemical stability of TiO2 nanotube layers provided by uniform Al2O3 coatings.

Thus, the present results, especially for the thinnest Al2O3 coating (1 nm), are very useful and promising for practical applications of the nanotube layers. As-treated TiO2 nanotube layers: (i) maintain anatase structure (more favorable for photovoltaics and photocatalysis than rutile) in the tubes over a very broad temperature range, (ii) possess significantly improved charge separation on the interface with various electrolytes (especially because electrons can tunnel to TiO2 via Al2O3 coatings thinner than ≈2 nm65), (iii) possess strong mechanical integrity, and (iv) provide extremely good stability in strongly acidic environments. All these features pave favorable way for the functionalization of TiO2 nanotube layers by secondary materials. It is foreseen that additional materials, such as various oxides, nitrides, sulfides, etc., may further expand the range of applications of TiO2 nanotube layers. Thermal and chemical stability of Al2O3-coated TiO2 nanotube layers can extend the utilization of nanotube layers for catalytic applications and sensing of gases (such as CO, NOx, CH3CH2OH, H2, and O2) at high temperatures and/or in harsh acidic environment, so far unfeasible for uncoated TiO2 nanotube layers counterparts. In parallel, membranes composed of ultrahigh aspect ratio TiO2 nanotube layers that have been used for photocatalytic or flow-through experiments51 may be prone to mechanical instabilities. Thus, they could greatly benefit from a thin Al2O3 coating to become mechanically more robust.

**CONCLUSIONS**

In this work, effects of Al2O3 coating produced by ALD on the crystal structure, mechanical, and chemical properties of TiO2 nanotube layers were explored. Noteworthy improvement of the thermal stability upon annealing in air was revealed up to temperatures of 870 °C, even with an extremely thin Al2O3 coating (1 nm). In contrast to uncoated TiO2 nanotube layers (100 vol % rutile), a high fraction of anatase structure (83 vol %) was determined for Al2O3-coated (1 nm) TiO2 nanotube layers upon annealing at 870 °C, which is highly desired due to its optical and electronic properties for photovoltaic and photocatalytic applications. An enhanced hardness was revealed for Al2O3-coated TiO2 nanotube layers with a positive impact on the mechanical properties of nanotube layers. In addition, Al2O3 coatings provided to the TiO2 nanotube layers extremely good stability in extremely acidic environments of H3PO4 solutions with different concentrations. All in all, self-organized TiO2 nanotube layers coated with thin Al2O3 coatings yield superior thermal, chemical, and mechanical stabilities that will extend their application range to previously nonimaginable working environments.

**AUTHOR INFORMATION**

**Corresponding Author**

*E-mail jan.macak@upce.cz, Ph +420-466 037 401 (J.M.M.).

**ORCID**

Jan M. Macak: 0000-0001-7091-3022

**Notes**

The authors declare no competing financial interest.

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