



One-dimensional suboxide TiO₂ nanotubes for electrochemical applications

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ABSTRACT

This mini-review summarizes the recent research on the applications of anodic one-dimensional suboxide titania nanostructures with enhanced electrochemical properties by introducing atomic-scale defects into the titania systems. Due to the unique semiconductive properties of TiO₂ nanostructures, so far, the main focus of research has been on photocatalytic applications of this semiconductor. The limited conductivity of pristine anodized titania restrains the application of one-dimensional (1D) nanostructured TiO₂ as an electrode. However, recently published works present that suboxide TiO₂ nanotubes, due to the enhanced conductivity, are promising electrodes for electrochemical applications. In this mini-review, we highlight the unique advantages of defective TiO_{2-x} nanotubes as an electrode and address the recent electrochemical applications of 1D anodic TiO₂ nanotubes.

1. Introduction

Owing to the unique properties of self-organized nanostructured arrays of binary oxides, they have attracted considerable scientific and technological attention in the last few decades [1–3]. Self-organization was first reported for anodic oxidation of aluminum in 1936, leading to the formation of porous alumina structures

[4]. The work of Masuda and Fukuda [5] showed a highly ordered hexagonal array of alumina nanotubes using rigorous optimization of anodization parameters. Such anodized structures have been extensively used as templates for the fabrication of nanofibers and nanowires – a number of excellent reviews related to the synthesis methods and applications are available [6,7]. In 1984, Assefpour-Dezfuly et al. [8] reported on the formation of self-organized TiO₂ nanotubes via anodization. Their work was followed by Zwilling et al. [9] in 1999 and Grimes [10] in 2001. Since then, TiO₂ nanotubes have been recognized as promising materials so that the number of publications on TiO₂ nanotubes exceeded the ordered alumina nanostructures [11–13]. This is mainly due to the unique properties of TiO₂, namely a wide bandgap of 3.0–3.2 eV, non-toxicity, corrosion-resistance, and biocompatibility [1,11], which make it a suitable candidate for a wide range of applications such as photocatalysis [3,14], self-cleaning [15,16], solar cells [17], sensors [18], biomedical [19], electrochromic materials [20], and batteries [21].

Among the diverse growth techniques for nanotubes, anodization is favorable as it is an inexpensive and straightforward method to produce

highly ordered self-organized TiO₂ nanotubes with controllable dimensions and enhanced surface areas (See Fig. 1a-c). Recently, Chen et al. reported on the novel double-anode anodizing in two beakers using a wired anode and a wireless anode [22]. Since TiO₂ nanotubes directly grow on the metal substrates, a one-dimensional (1D) back-contacted structure forms during anodic growth and, more importantly, provides a back-contacted oxide electrode which is geometrically beneficial for improved charge collection efficiency (See Fig. 1d). As schematically shown in Fig. 1d, 1D nanostructures provide a direct path for e⁻ transport from the back contact toward the electrolyte, improve charge carrier separation, thus, enhance carrier collection efficiency. Despite the aforementioned advantages of 1D TiO₂ nanotubes, their application as an electrode is very limited. This is primarily ascribed to the inherent low conductivity of pristine TiO₂ due to its semiconductive nature. In the last few years, there have been some promising reports on enhancing the electrical conductivity of 1D TiO₂ nanotubes via various reduction treatments that enable the introduction of free e⁻ in the system. The research field on conductive TiO₂ for electrochemical functions is still fresh, and the fundamental understanding of the material's properties should be developed. There are a number of excellent reviews on reduced titania, with a focus on photocatalytic applications [23,24]. However, to the best of our knowledge, there is no review on the electrochemical applications of 1D suboxide TiO₂. It is worth noting that the use of suboxide titania as an electrode is reported in the form of Magneli phase with and without metal [25,26] decoration. Magneli phases, with the commercial name of Ebonex, are a substoichiometric composition of titanium oxides

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of the general formula Ti_nO_{2n-1} , (n is between 4 and 10) [27]. Magneli phases are produced from titanium dioxide powder. Typically, the powder is heated to temperatures exceeding $1000\text{ }^\circ\text{C}$ and cooled down to ambient temperature in a controlled hydrogen atmosphere. To fabricate a titania oxide Magneli phase electrode, the typical steps of electrode preparation from a powder are followed. The reduction is carried out using hydrogen gas to obtain monophasic Ti_4O_7 at temperatures above $1000\text{ }^\circ\text{C}$. The continuing development of Ebonex electrodes is studied by Walsh and Wills [28]. However, a notable disadvantage of Ebonex electrodes is that they are fabricated from nanoparticles; thus, an additional step to use them as an electrode is needed. More importantly, the nanoparticles are oriented in a random direction on the surface, which leads to charge losses due to a chaotic electron diffusion pattern to the back contact. Thus, evolving a strategy to form a stable nanostructured electrode with a straightforward method is of great importance. In this context, the direct use of reduced anodic 1D TiO_2 nanotubes, which have higher conductivity compared to pristine TiO_2 (due to the presence of free electrons as a result of defect formation) and benefit from a straight charge transfer path is indeed advantageous.

To gain a deeper insight into the concept of defect engineered TiO_2 nanostructures, the various types of defects in TiO_2 , strategies to form the defects, mechanism of defect formation, and methods of characterizing these defects are discussed in the [supplementary information](#).

This mini-review will address state of the art in defective back contacted 1D TiO_2 nanostructures and their promising implementation as an electrode for electrochemical purposes.

2. Applications of 1D reduced TiO_2 nanotubes as an electrode

More recently, reduced TiO_2 nanotubes showed a promising performance as an electrode for energy conversion [29] and energy storage applications. TiO_2 nanotubes as an electrode have numerous advantages: i) 1D TiO_2 nanotubes formed via anodization are directly back contacted to a conductive metal (Ti) foil. The direct back contact to a conductive substrate eliminates the complicated step of electrode preparation from powder materials, which arises ambiguity on the influence of binder and the support material on the performance of the electrode as a whole, ii) TiO_2 nanotubes as an electrode are able to provide a high active surface area which is an asset for catalytic applications, iii) anodic TiO_2 nanotubes are stable in acidic and basic environments, and iv) 1D TiO_2 nanotubes provide a direct charge pathway in comparison to the powder-based electrodes. However, the main

drawback of TiO_2 is its low electrical conductivity due to its inherent semiconductive nature. It has been shown that introducing defects via optimum reduction treatment can improve the conductivity of TiO_2 to a great extent [30]. It is widely believed that the presence of the point defects, namely Ti^{3+} /oxygen vacancy in the TiO_2 structure, introduce mid-gap energy states close to the conduction band and valence band, thus decreasing the bandgap of titania. As a result of the bandgap narrowing, light absorption is extended toward the visible range of the spectrum, thus affecting the optical properties of titania. As a rule of thumb, a higher density of point defects leads to a darker color due to the formation of states $0.8\text{--}1.2\text{ eV}$ below the conduction band of TiO_2 , thus enhancing the absorption in the visible range of the light spectrum [31]. Depending on the method and degree of reduction, i.e., the formation of point defects in TiO_2 , the color is distinguished as varied tones of yellow, orange, grey, blue, or black (see Fig. 2a,b for TiO_2 nanopowders and TiO_2 nanotubes, respectively) [32]. The enhanced visible light absorption for the defective TiO_2 has received great attention for photocatalytic applications, and excellent reviews are available in this area of research [33,34]. However, as pointed out earlier, there has also been a significant enhancement in conductivity of the TiO_2 structure upon reduction treatment which we believe has been in the shadow of enhanced visible activity.

Remarkably, in addition to the effect of point defects on the conductivity of the structure, it was shown that certain types of point defects (see various types of point defects in titania in Fig. 2c), in TiO_2 , namely surface-exposed Ti^{3+} are the active sites to anchor single-atom catalysts [35,36], which can further improve the performance of the defective TiO_2 as an electrode, especially when it is used in catalytic applications.

The improved conductivity in the TiO_2 structures via optimum reduction treatment with no influence on the morphology of the structure (See TEM and SEM images of nanotubes after reduction in Fig. 2d) can open up a new field in electrochemical applications. Therefore, this section mainly focuses on the novel function of defective TiO_2 in electrochemical applications.

In the following, we discuss the areas of research where reduced TiO_2 nanotubes with or without decoration as an electrode have a significant effect on the system's performance. Additionally, the potential of defective TiO_2 nanotubes as an electrode with considerable improvement in the efficiency of the reactions is elaborated. Within this framework, recent research on the use of suboxide TiO_2 nanotubes as an electrode in water splitting, fuel cells, CO_2 reduction, Li-ion batteries, and supercapacitors are discussed.

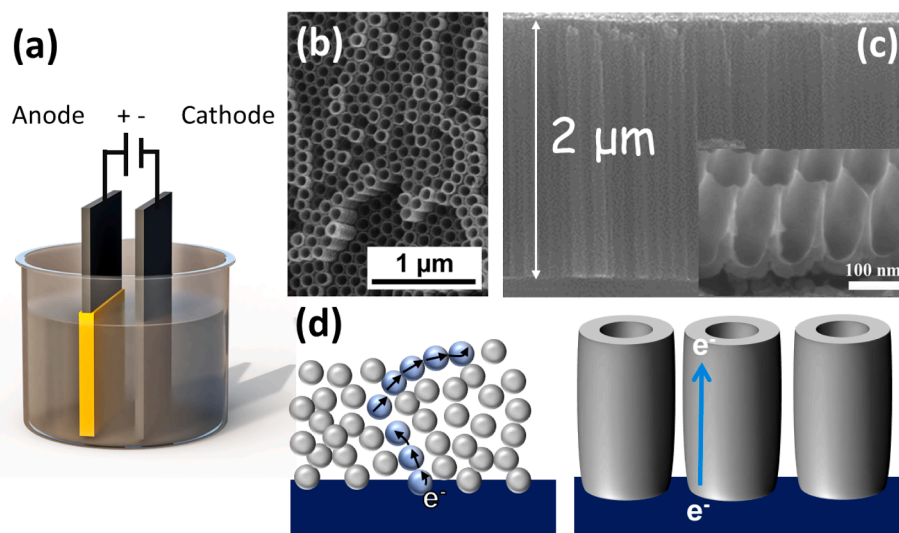


Fig. 1. (a) schematic of an anodization set-up; (b) top surface and (c) cross-section SEM images of high aspect ratio anodic titania formed by anodization and (inset c) low aspect ratio; (d) schematic of charge path for nanotubes compared to nanoparticles. Fig. (b) is reproduced from Ref. [1] with permission from John Wiley & Sons. Fig. (c) is reproduced from Ref. [3] with permission from Elsevier. Fig. (c) inset is reproduced from Ref. [60] with permission from American Chemical Society.

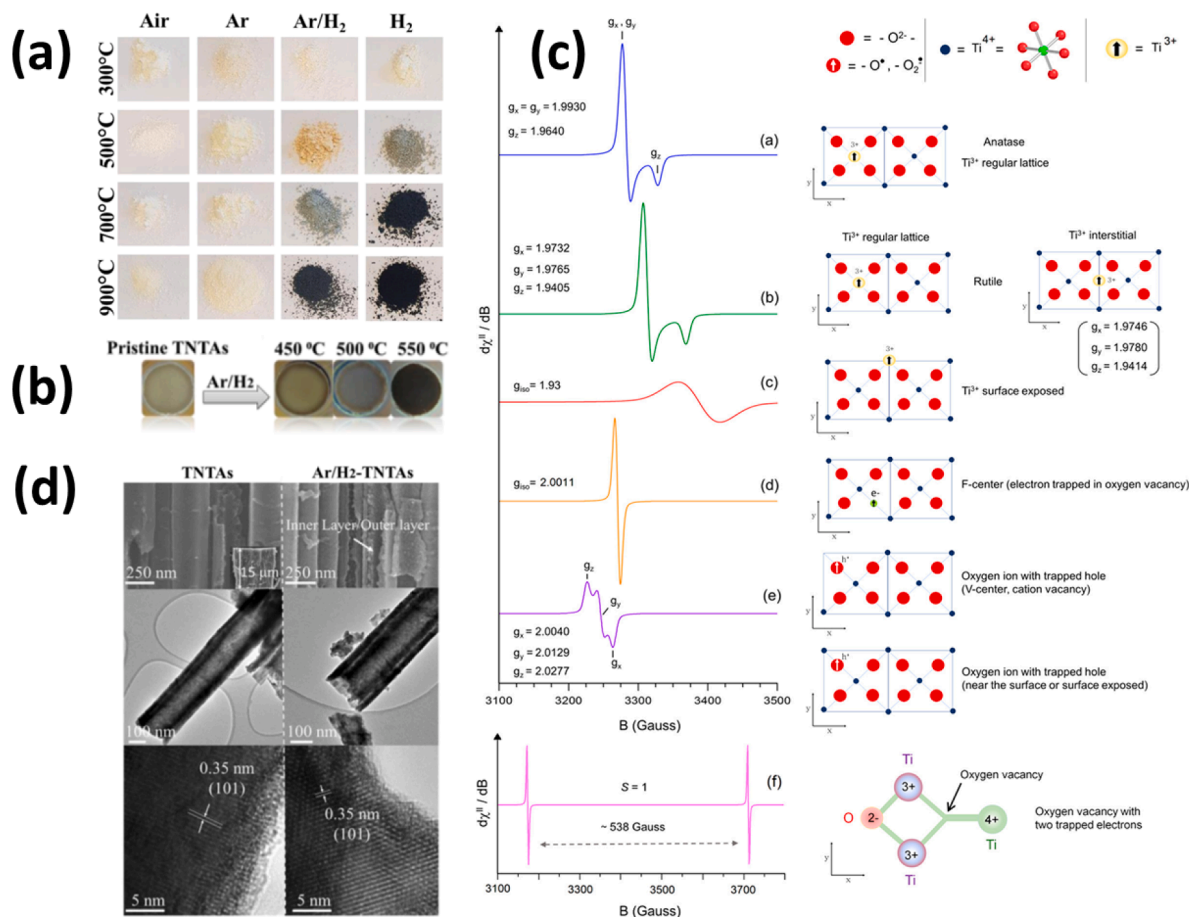


Fig. 2. optical images of the color changes in reduced TiO_2 (a) nanopowders and (b) nanotubes; (c) simulation of EPR spectra of spin-containing centers; (d) SEM and HRTEM images of the reduced TiO_2 nanotubes compared to pristine TiO_2 . Fig. (a) is reproduced from Ref. [61] with permission from the Royal Society of Chemistry. Elsevier. Fig. (b,d) is reproduced from Ref. [30] with John Wiley & Son's permission. Fig. (c) is reproduced from Ref. [24] with permission from the American Chemical Society.

Water splitting: In 2015, Lačnjevac et al. [37] reported on RuO_x decorated TiO_2 nanotubes as an electrocatalyst for H_2 evolution reaction. In their work, they reduced the TiO_2 nanotubes electrochemically at a constant current of -5 mA for 1 h. A significant color change to black was observed for the electrochemically hydrogenated samples. Additionally, the cathodically hydrogenated samples resulted in four orders

of magnitude higher concentrations of electron donor Ti^{3+} states; thus, a significant improvement of capacitive voltammetric response was observed. They proved that when such a structure is decorated with RuO_x nanoparticles via an ion exchange approach, it can deliver an extremely active electrocatalyst for the hydrogen evolution reaction (HER), with 560 mV lower H_2 generation overpotential than the

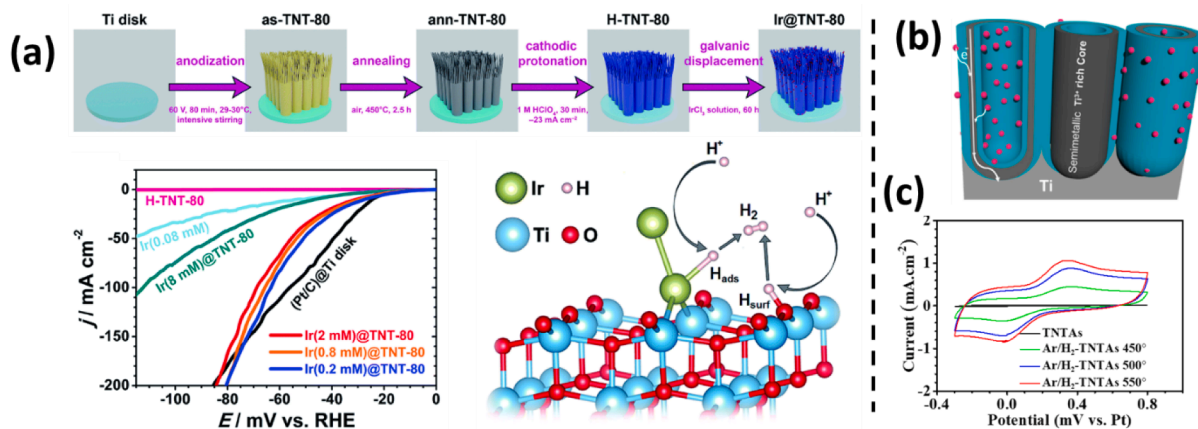


Fig. 3. (a) schematic illustration of the electrochemical reduction of TiO_2 nanotubes followed by Ir decoration, polarization curves of the Ir decorated TiO_2 nanotubes and H_2 generation reaction pathway, (b) schematic of RuO_x decorated reduced TiO_2 nanotubes and cyclic voltammograms of the reduced tubes as a scaffold for supercapacitor applications. Fig. (a) is reproduced from Ref. [38] with permission from the Royal Society of Chemistry. Fig. (b) is reproduced from Ref. [59] with permission from Elsevier and Fig (c) is reproduced from Ref. [30] from John Wiley & Sons.

compact TiO₂ structure. In a remarkable approach, Pd nanoparticles were deposited on the cathodically hydrogenated TiO₂ nanotube's wall with straightforward galvanic displacement. The results of this research demonstrate a significant improvement in the H₂ evolution reaction activity. The authors assigned the improvement of the Pd decorated TiO₂ nanotubes' performance to the unique properties of the 3D nanostructure that can provide an abundance of Pd active sites and at the same time can prevent anodic degradation of the Pd catalyst [37]. Recently, with a similar approach, protonated TiO₂ nanotubes were used to support Ir decoration for electrocatalytic H₂ generation [38]. The authors believe that the galvanic decoration of reduced TiO₂ nanotubes as an HER electrocatalyst paves the way towards developing a highly efficient yet affordable class of catalysts (see Fig. 3a). Despite the reports mentioned above on the high efficiency of 1D reduced TiO₂ for HER its performance for oxygen evolution reaction (OER) is challenging [39]. This is mainly due to the large overpotential required for the OER. In this regard, Harynski et al. [40] reported on the Ni-decoration of free-standing TiO₂ nanotubes. They showed that Ni decorated TiO₂ nanotubes increase the charge carrier concentration and consequently could enhance the overall water splitting efficiency with enhanced influence on the OER.

There are several reports on TiO₂ nanotubes decorated with metals such as Pt [41], Pd [42], Au [43], Ag, and Cu [44] with improved overall water splitting performance. We believe that employing reduced TiO₂ 1D structures, i.e., the more conductive material, as a scaffold for anchoring active noble metal single atoms, such as Ir, Ru, Pt, Pd, Au, Ag, and Cu, in the defects can provide promising, high efficiency and stable electrodes for overall water splitting.

CO₂ reduction: The primary step in the CO₂ reduction reaction (CO₂RR) is CO₂ adsorption. However, due to the strong neutrality of CO₂ gas and lack of active sites on TiO₂ nanotubes, the efficiency of CO₂RR on TiO₂ tubes is limited [45]. Defective 1D-back contacted anodic TiO₂ nanotubes can be a potential electrode for electrochemical CO₂ reduction. This is mainly due to the fact that on the one hand, the enhanced concentration of oxygen vacancy and Ti³⁺ centers can act as active sites for CO₂ adsorption, and on the other hand, they can provide anchoring sites for single atoms (namely, noble metals) that can decrease the energy barrier of CO₂RR [46]. Surface defect engineering on TiO₂ has been recently introduced by Rawool et al. [45] as an effective method to increase the efficiency of photocatalytic CO₂RR. Ramesha et al. [47] reported on the role of Ti³⁺ on the electrocatalytic reduction of CO₂. They suggest that the binding of CO₂ to Ti³⁺ sites decreases the potential necessary for the reduction. In this study, a thin film of TiO₂ coated on a glassy carbon was used as the electrode. Gu et al. [48] used TiO₂ nanotube as a support electrode for immobilization of cobalt porphyrin for electrocatalytic CO₂ reduction in an aqueous environment. The results show that due to the high surface area of the TiO₂ nanotubes electrode, the concentration of active sites is almost two times higher than the cobalt porphyrin drop-casted on a carbon electrode and leads to a significantly improved reduction current in comparison to the unmodified TiO₂ nanotubes. Considering the results of the last two reviewed papers in electrochemical CO₂ reduction, we believe that combining the two strategies of nanotubular structuring and Ti³⁺ defects engineering has a synergistic effect on providing an efficient electrode for enhanced electrochemical CO₂ reduction.

Li-ion batteries: As a result of high stability and low cost, TiO₂ nanostructures have been recently nominated as an ideal alternative for the conventional graphite anode of Li-ion batteries [49]; however, their application toward industrialization is limited due to low electrical and Li⁺ conductivity [50], low capacity [51], and distortion during Li⁺ intercalation/de-intercalation [52]. Different strategies have been employed to overcome these limitations. Zhang et al. [53] prepared TiO₂ nanoarrays coated with an Au thin film as anode material for Li-ion batteries and stated that Au remarkably increases the electrical conductivity; however, its low capacity is still a challenge, compared to graphite anodes. To increase the capacity of TiO₂ anodes, carbon

incorporation into TiO₂ has been proposed by Wang et al. [54], where they synthesized porous TiO₂ to trap C atoms through hydrothermal treatment. Patil et al. [55] reported that oxygen vacancies in the reduced TiO₂ nanoparticles lead to faster kinetics and easier reinstitution of Li⁺ during intercalation/de-intercalation. A similar strategy has been reported elsewhere [56]. Kirchgeorg et al. [57] investigated the important factors influencing the Li storage capacity in TiO₂ nanotubes as an electrode. The studied parameters include the presence of the initiation layer on top of the tubes and the double-wall morphology of the tubes with the inner C-rich layer. We believe that due to the unique features of the 1D-back contacted scaffold of reduced TiO₂ nanotubes, which show improved conductivity and surface area, such defective structures can be a promising candidate to minimize the mentioned limitations of TiO₂ application in Li batteries.

Supercapacitors: As an ideal device for electrochemical energy storage with ultra-high capacity, excellent cycling stability, and high power density, supercapacitors attracted considerable attention in recent decades [58]. RuO₂ with a capacity of 1400–2000F·g⁻¹ has been introduced as one of the most favorable materials for supercapacitors; however, the high cost and agglomeration issues hinder its wide marketable use. To overcome this issue, Mohajernia et al. prepared 1D nanoarrays of reduced TiO₂ nanotubes decorated with RuO₂ nanoparticles [59]. A significant enhancement in the electrical conductivity of the TiO₂ nanotube scaffold was obtained. Upon decoration of the conductive scaffold with a very low amount of RuO₂ (0.048 mg·cm⁻²), a capacitance of 1297F·g⁻¹ was achieved (see Fig. 3b). In our opinion, rigorous defect engineering of TiO₂ as a scaffold for uniform decoration with RuO₂ can be a feasible and effective way to reach higher capacities and electrical conductivity.

In all the research mentioned above, the key aspects for the improved performance of the system as a result of using reduced 1D TiO₂ nanotubes as an electrode are a) efficient charge transfer due to the 1D structure, b) efficient charge collection due to a direct back contact to a metal foil, c) enhanced conductivity due to the presence of free electrons in the defective structure, d) presence of defects as preferable sites for reactant adsorption and single atom decoration, and e) high surface area.

3. Conclusion

In the present mini-review, the role of defects on the properties of TiO₂, as well as strategies to produce atomic-scale defects, mechanisms of defect formation, techniques for analyzing these defects, and the fascinating features of suboxide TiO₂ nanotubes for electrochemical applications are reviewed. Based on this mini-review, our understanding is that the two parameters of i) optimum reduction treatment that introduces atomic-scale defects, namely, Ti³⁺/oxygen vacancies, into the system with a specific density and ii) beneficial geometrical features of TiO₂ nanotubes are the keys to the enhanced charge collection efficiency, which result in the development of promising electrodes for electrochemical applications. In this mini-review, our aim is to bring to attention the overlooked aspect of using defective TiO₂ as an electrode that should be explored more thoroughly to improve the performance of the suboxide TiO₂ for this purpose. To reach the performance comparable to current commercialized electrodes, fundamental studies on the types and roles of defects produced by various reduction treatments must be undertaken to find out the most optimum density and type of defects for the intended application. In this context, one approach is studying the role of defects in various polymorphs of TiO₂ for a specific application. Another leap is combining the experimental results with DFT calculation to increase the understanding of the impact of the defects on the performance of the system and, more importantly, predict the reactions' behavior. Eventually, the reduced anodic 1D TiO₂ nanostructure is a promising candidate to be used as an electrode in clean energy technologies.

CRediT authorship contribution statement

S. Hejazi: Writing – original draft, Writing – review & editing. **S. Pour-Ali:** Writing – original draft, Writing – review & editing. **M.S. Killian:** Writing – review & editing, Funding acquisition. **S. Mohajernia:** Conceptualization, Writing – original draft, Writing – review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.elecom.2022.107246>.

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