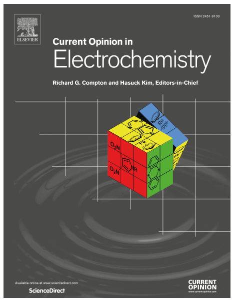

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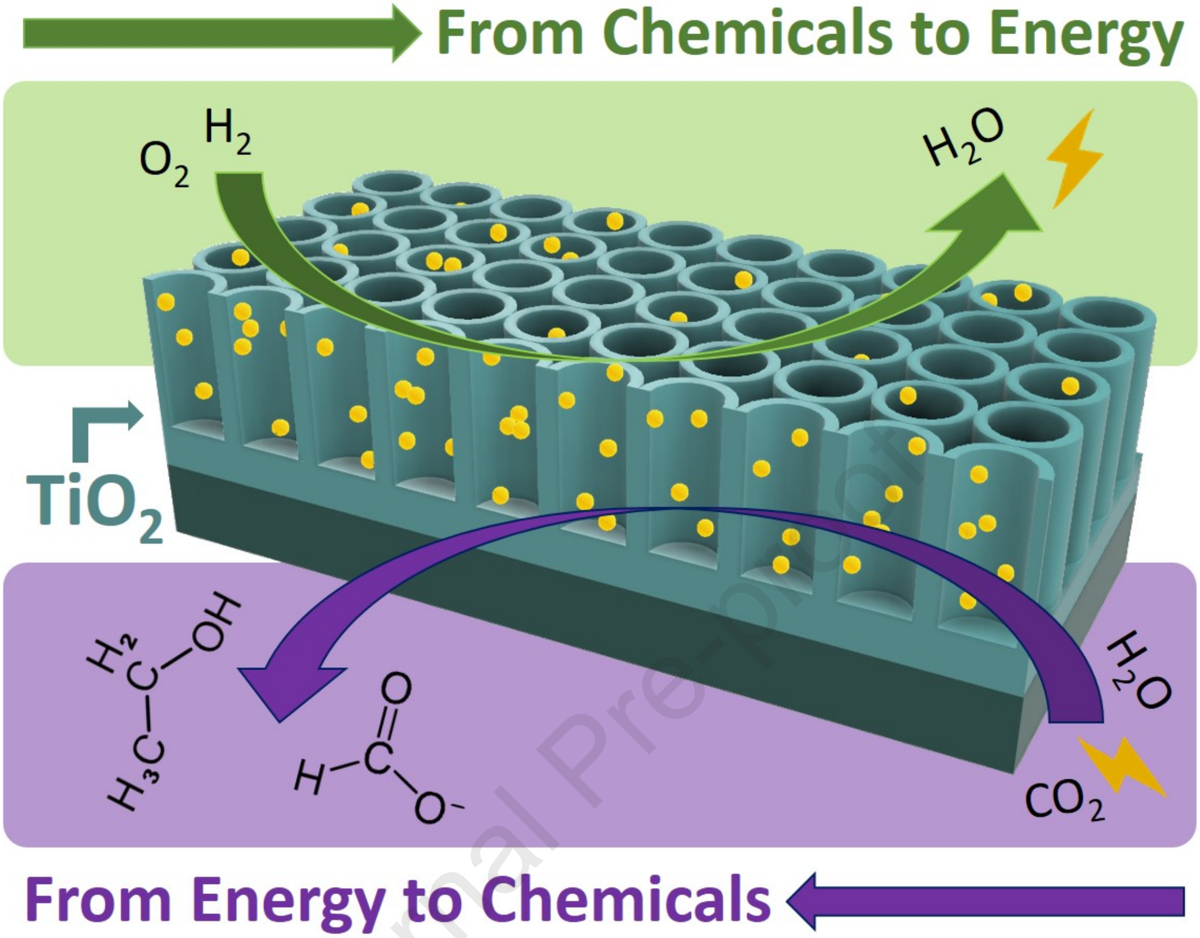
From Chemicals to Energy
O_2
H_2
H_2O
TiO_2
H_2O
CO_2
H_3C–CH_2–OH
$HCOO^-$
From Energy to Chemicals

Titanium dioxide nanomaterials in electrocatalysis for energy

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Abstract

Over the last two decades, researchers have found many strategies to obtain high surface area nanostructured titanium dioxide. These nanostructures have recently found application as supports for the fabrication of electrodes for electrochemical energy conversion and storage devices. The properties that make titanium dioxide appealing for these applications are: i) stability in a variety of conditions relevant to electrocatalysis, ii) electronic conductivity, iii) synergistic effects with metal catalysts. The work splits TiO_2 nanomaterials into two classes: i) powders and ii) embedded nanoarchitectures (e.g. titania nanotubes on titanium support). We give an overview of the latest applications, with a special emphasis on fuel cells, electrolysis, and carbon dioxide electro-reduction. We conclude with a list of the research needs that, in the opinion of the authors, will support the exploration and consolidation of the use of titania in electrocatalysis for energy.

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Keywords: Titanium Dioxide, Electrocatalysis, Energy, Nanotubes, Nanotechnology

Introduction

Titanium dioxide (Titania) has dominated photocatalysis since the discovery of the phenomenon in the early 1970s [1]. Since then, researchers have developed a variety of methods to tune the nanostructure and the composition to optimize the photocatalytic efficiency [2]. Recently, titania has generated a consistent interest as a material for “dark” electrocatalysis for the production and the conversion of renewable energy. This paper focuses on the latter subject and briefly reviews the properties of titania relevant to its application to electrochemical energy conversion and storage: i) resistance to corrosion, ii) electronic conductivity, iii) synergistic effects with active metals. This paper also discusses some of the most recent results, classifying titania nanomaterials in two classes: i) powders and ii) embedded nanoarchitectures. We believe that embedded nanoarchitectures will become increasingly more popular in the future for two significant facts, ease of handling and reduced risk for humans and the environment connected to the emission of nanomaterials. [3]

Material properties relevant to electrocatalysis

Titanium (IV) oxide has three crystalline forms: anatase, rutile and brookyte. Anatase is by far the most exploited in photocatalysis for its electron properties, but rutile and amorphous TiO_2 have found application in electrocatalysis [4]. Often, the low-temperature synthesis of oxides leads to the formation of titanates or amorphous phases. These phases that can easily be converted into crystalline phases chemical and/or thermal treatment. Titania can easily be fabricated in nanostructures with high surface area [5]. This enables the dispersion of catalysts nanoparticles to provide high Electrochemically Active Surface Areas (ECSA). Table 1 reports some recent examples of high surface area titania nanomaterials. Remarkably, Pt ECSAs up to 232 m^2 g^{-1}on titania support have been reported.

The conductivity of stoichiometric titanium dioxides is generally low and unpractical for application in electrocatalysis. The most common strategies to improve the conductivity are: (i) the use of sub-stoichiometric titanium oxides with formula TiO_{2-x} [4,6,7]; (ii) Doping with metals having atomic radii similar to Ti^{4+}, e.g. Nb^{5+} or Mo^{6+} [8,9] and (iii) Blending titania with electronically conductive materials such as carbon or PANI. All these strategies have been applied in the fabrication of electrocatalysts.

Titanium dioxide has a strong promoting effect on many reactions of interest in electrochemical energy conversion and storage. Promotion is due to the hypo-d-electron character of that generates strong interactions with hyper-d-electron character metals, such as platinum [10]. This interaction produces a contraction of the Pt-Pt distance, the inhibition of hydroxyl chemisorption and the shift of the formation of surface PtOH toward positive potentials. The combination of these effects favours the interaction with molecular oxygen in the Oxygen Reduction Reaction (ORR). The effect of titanium dioxide on the formation of Pt-OH species has been shown experimentally in [11]. Apart from the ORR, synergistic effects between titanium oxides and Pt also promote the oxidation of small organic molecules [12,13]. The evidence of Strong Metal to Support Interaction with dramatic effects in electrocatalysis have also been reported [14] (●●).

The synergy between the oxide and catalysts particles also benefits stability. It has been found that for Pt on TiO_2 a static polarization @ 0.55V led to a 13% decay in ORR current density after 1 h while for a conventional Pt/C the current density dropped by 80% [11]. Synergistic effects may also increase the tolerance to poisoning species with significant CO poisoning of Pt anodes reduction in direct methanol fuel cells [6,15]. The catalyst stability is also affected much by corrosion. Titania is relatively stable in many environments relevant to electrocatalysis. The Pourbaix diagram of Ti show that titania is stable from highly oxidizing to mildly reducing conditions in acids, including potential fields in which carbon is not stable. However, titanium oxides can dissolve in reducing condition in acids and practically at any potential in concentrated alkali. Significant degradation of titania nanostructure at pH 14 has been demonstrated [16] (●). Moreover, degradation can happen in the presence of limited amount of strongly complexing agents, even down to 10-15 ppm in the case of free fluoride. Remarkably, better durability of the TiO_2 catalysts has been achieved by the addition of Nb^{5+} or Mo^{6+} [8,9]. Tantalum has also been proved to enhance the stability of the performance of TiO_2 in PEMFCs [17].

Despite of the thermodynamic consideration, titania degradation may depend on the nature of the oxide and the variability of the environment and stability can be affected by the complex environment of real-world devices. Accordingly, an evaluation of the long-term stability in the relevant operating conditions is necessary.

Titania nanomaterials: powders

Figure 1 shows a few examples of titania nanomaterials with different dimensionality: 0D materials, e.g. nanospheres, [18] fig. 1a) and 1D materials (e.g. nanotubes [19] or nanofibers [8,9] fig 1b).

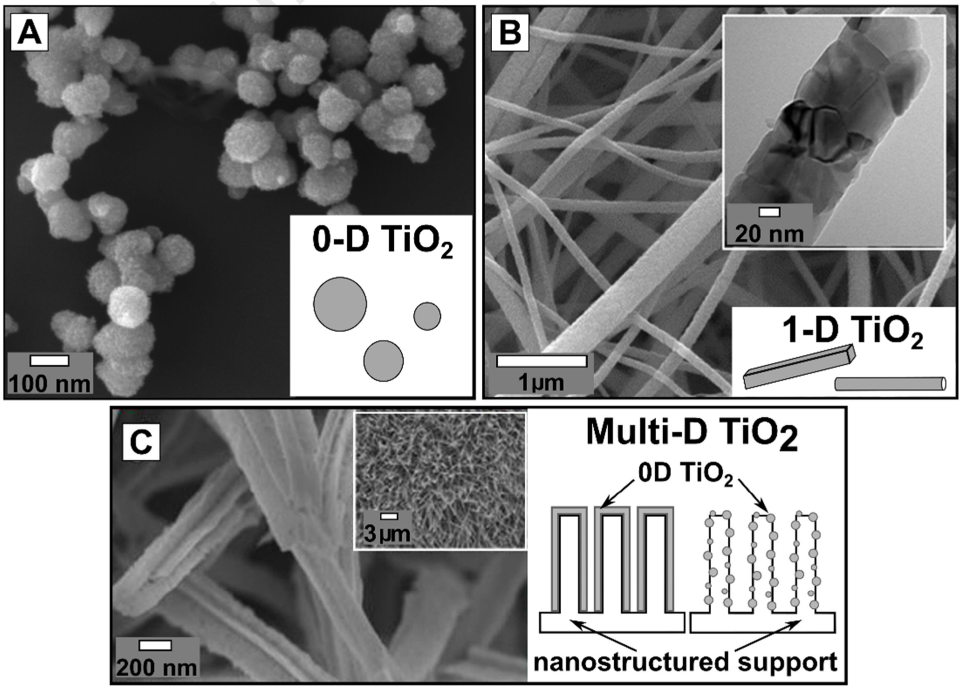

Figure 1: (A) 0D titania nanostructures used as cathodes for promoting the oxygen reduction reaction; figure adapted from ref [18]. (B) TiO_2 nanofibers as an example of one-dimensional nanostructured titania employed for promoting

ORR; figure adapted from ref [9]. Multidimensional materials based on nanostructured conductive supports (CuO nanowires arrays) decorated with zero-dimensional titanium dioxide for promoting hydrogen evolution reaction; figure adapted from ref [20] (●).

These materials show a large surface area that allows the deposition of active phases with high Electrochemically Active Surface Area (ECSA) to have high activity per unit mass or volume of catalysts [21]. Table 1 shows a brief summary of the ECSA and BET reported in the recent literature.

Table 1: ECSA values reported in the recent literature

Catalyst	Application	BET area	ECSA area	Ref.
IrO_2-TiO_2 nanocomposite	Hydrogen Evolution Reaction	278.8 m^2 g^{-1}	22.85 mC cm^{-2}	[22]
Pt-TiO_2-PANI	Methanol Oxidation Reaction	/	41.24 m^2 $g^{-1}{}_{Pt}$	[23]
Pt@Nb doped TiO_2 nanofibers	Oxygen Reduction Reaction	16 m^2 g^{-1}	36 m^2 $g^{-1}{}_{Pt}$	[8]
Pt@TiO_2 doped CNTs	Oxygen Reduction Reaction	32.9 m^2 g^{-1}	52.1 m^2 $g^{-1}{}_{Pt}$	[24] (●●)
Pt@TiO_2 microspheres	Oxygen Reduction Reaction	/	25.2 m^2 $g^{-1}{}_{Pt}$	[25] (●)
Pt@ Graphene nanosheets – TiO_2 nanoparticles doped	Methanol Oxidation Reaction	/	30.7 m^2 $g^{-1}{}_{Pt}$	[26]
PtPd@TiO_2 nanoparticles	Methanol Oxidation Reaction	/	74.63 m^2 $g^{-1}{}_{metal}$	[27]
Pt@TiO_2 nanoparticles	Methanol Oxidation Reaction	/	240.2 m^2 $g^{-1}{}_{Pt}$	[27]
Pt@CNT-TiO_2 microspheres	Oxygen Reduction Reaction	130 m^2 g^{-1}	31.3 m^2 $g^{-1}{}_{Pt}$	[28]
Pt@TiO_2-C-PANI	Methanol Oxidation Reaction	/	49.6 m^2 $g^{-1}{}_{Pt}$	[23]
Pt@TiO_x	Oxygen Reduction Reaction	/	22 m^2 $g^{-1}{}_{Pt}$	[7]
PtRu@C-Mo doped TiO_2 nanotubes	Methanol Oxidation Reaction	/	69.1 m^2 $g^{-1}{}_{metal}$	[29]
TiO_2 nanoparticles	Oxygen Reduction Reaction	83	/	[18]
Pt@TiO_2-PANI core-shell nanowires	Oxygen Reduction Reaction	/	100.56 m^2 $g^{-1}{}_{Pt}$	[30]
TiO_2 nanoparticles/C	Biofilm anodic support for Microbial Fuel Cells	435.2 m^2 g^{-1}	/	[31]

Carbon is frequently mixed with to titania to confer electronic conductivity. Carbon nanotubes blended together with titania and platinum nanoparticles [28] or coated with thin titania films have been reported [24(●●),32]. In [24] (●●) it was also shown that titania containing catalysts experience significant degradation after 10000 start and stop cycles, with an unclear degradation mechanism. Blending titania with graphene, delivered outstanding activity toward methanol oxidation (3464 mA mg_{Pt}^{-1} vs 988 mA mg_{Pt}^{-1} for Pt/GNs and 1018 mA mg_{Pt}^{-1} for Pt/C) [26]. Mixing TiO_2 with PANI has also been reported to produce inks that can be spread directly onto the surface of Polymer Exchange Membranes (PEMs). An H_2/O_2 fed PEMFC working at 70°C equipped with a cathode based on TiO_2@PANI (core@shell) nanotubes arrays decorated with Pt delivered an ASR of 0.071 $\Omega*cm^2$, with 774 mW cm^{-2} peak power density compared to 699 mW cm^{-2} for a Pt/C based fuel cell [19,27,30,33]. The amino groups in the polymer work as nucleation centers for Pt nanoparticles [34], and result in methanol oxidation activity of 640 mA mg_{Pt}^{-1} in 0.5M H2SO4 compared to the 430 mA mg_{Pt}^{-1} delivered by a cell equipped with Pt/TiO_2-C [23]

Methanol oxidation is promoted by the synergistic effects between TiO_2 and noble metal catalysts. Titania promotes the conversion of adsorbed CO intermediates to CO_2 during alcohols oxidation. [32] shows that in Pt/TiO2-PTP (perylene-3,4,9,10-tetracarboxylic acid-doped PANI) compound the ratio of the forward and backward peak intensity in the CV for methanol oxidation is 2.8 compared to 2.6 for the Pt/PTP benchmark. Remarkably, the $I_{forward}/I_{reverse}$ ratio remains unchanged after 100 scans showing a high tolerance to poisoning [27,34].

The photochemical carbon dioxide conversion to fuels (CO, HCOOH, CH_4 and C1-C2 liquid fuels) exploits photocatalysis with titania [35]. However, photocatalysis has limited efficiency and needs large surface areas to achieve significant productivity. [36] CO_2 “dark” electroreduction (CO_2 Reduction Reaction, CO_2RR) overcomes these limitations feeding reactors with renewable electricity; [36,37]. CO2RR has the advantage of employing electrode architectures, similar to PEMFCs and water electrolyzers. [37] Titania based catalysts are promising candidates for CO_2RR as the synergistic effects enhance CO_2RR activity and selectivity [21][38] (●). Ti_3O_5 outperforms TiO_2 in the reduction of carbon dioxide to CO and formate in a PEMFC like cell. The faradic efficiency for the production of CO @ -2.5V and $HCOO^-$ @ -2.3V were 7% and 10% for Ti_3O_5 and 3% and 3% for TiO_2, with maximum partial current densities of -1.5 mA cm^{-2} and -2 mA cm^{-2} for CO and $HCOO^-$ on Ti_3O_5 and -0.5 mA cm^{-2} for CO and $HCOO^-$ on TiO2 all at -2V. [39]

Titania nanomaterials: embedded nanostructures

Embedded titania nanostructures can be obtained by the strong anchoring of titania nanoparticles, nanotubes, and fibers onto nanostructured conductive supports arrays. This is the case of the growth of amorphous TiO_2 on CuO nanowire arrays (Fig. 1c) [20] (●) or of the deposition of titania quantum dots (0D TiO_2) on cobalt nanotubes arrays with a carbon nanofiber core [40]. The resulting catalysts have a 3D open structures that is excellent for water electrolysis for the limited formation of bubbles at the catalyst surface. [20(●),40,41(●)]. However, the most spectacular result of TiO_2 embedded nanostructure fabrication was the introduction of titania nanotube arrays (TNTA) grown by anodization. The first TNTAs were reported by Zwilling and co-workers in 1999.[42,43] These nanotubes, grown from water HF electrolytes, have a length up to 500-600 nm. [42,44,45] TiO2 nanotube layers with thicknesses higher than 2 μm can be obtained using NaF or NH_4F [46–49], while moving to organic solvents (e.g. ethylene glycol), produced nanotube lengths up to 1000um[50]. Two-step anodization result in hexagonally ordered arrays of TiO2 nanotubes [51] The control of the diameter of the nanotube is also possible. High voltage anodization delivers nanotubes with diameters up to 680-750 nm from an ethylene glycol electrolyte, while CH_3COOH/ NH_4F electrolytes produce diameters down to 20nm [52]. Comprehensive analysis of the relation between such parameters to the geometry and size of TNTAs has been reported.[53–55]. The use of TNTAs as support in electrocatalysis has delivered outstanding performance in the oxidation of alcohols in alkaline environments (8.96 A mg_{Pd}^{-1} CV peak) [55]. Despite the good performance, TNTAs grown on bulk titanium could not be used to fabricate membrane electrode assemblies for fuel cells and electrolyzers.

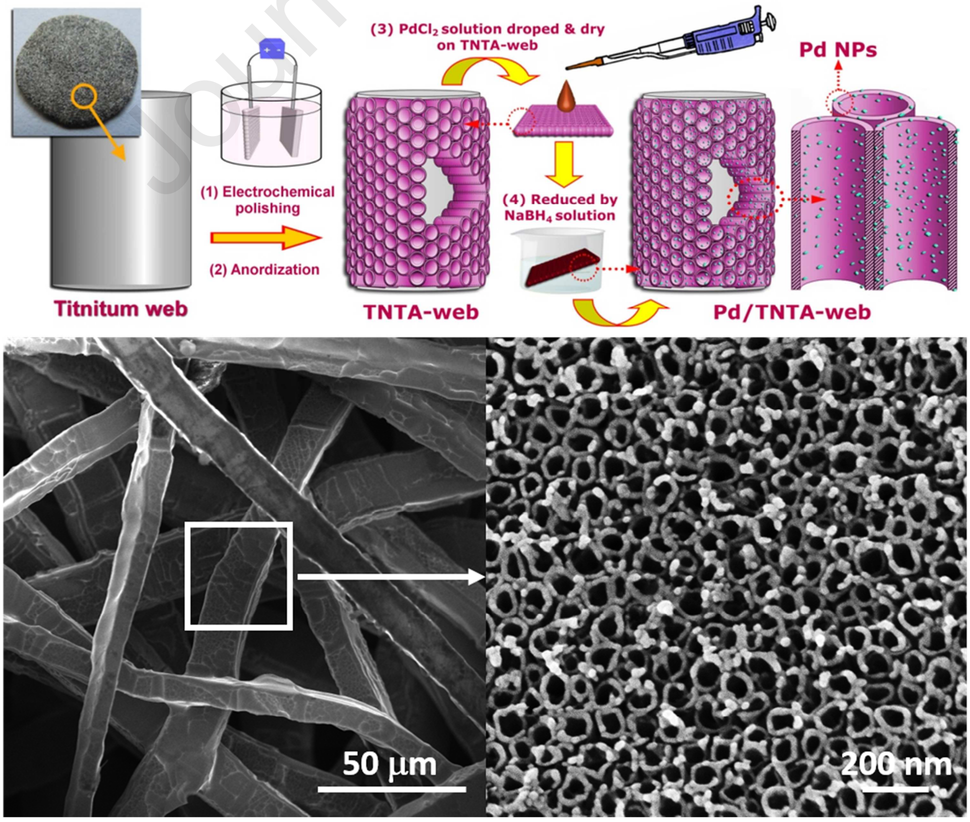

Figure 2. Scheme of the Pd/TNTA-web electrode preparation process along with a sample of the structure

To overcome this limitation, a new 3D architecture TNTA with dual scale porosity that allows the flow of solutions through the material has been proposed. Fig 2 shows the concept of fabrication. A titanium non-woven web (20µm fibers) is the substrate for the anodization that is followed by the addition of catalysts nanoparticles. [56] Accordingly, the system is completely carbon free[57]. The elimination of carbon is possible because the 3D TNTA have good electronic conductivity because the core of the fibers remains metallic. Membrane Electrode Assemblies (MEAs) can be fabricated by sandwiching a membrane between the 3D TNTAs. These MEAs do not need binders, with high utilization of the catalyst and excellent mechanical stability for easy handling and resistance to bubbling in electrolysis. The drawback is the thickness that exceeds that of conventional catalytic layers (100 µm vs. 10 µm), a fact that hampers the use in gas-feed fuel cells and electrolytic systems. A strategy to overcome this limitation should include the surface functionalization of titania with sulphate or phosphate groups to confer ionic surface conductivity and the use of thinner fibers (e.g. from 20 µm to 5 µm) with a potential reduction of the thickness of the catalyst layer to 25 µm. Functionalization may also be introduced to graft single site catalyst at the titania surface to provide ultra-low PGM loading as shown in [58,59] for carbon supports. The embedded 3D TNTA sustain high mass transport rate, generating high current densities. A major result in their application was the construction of an alkaline membrane electrolyzer that delivered a current density of 1 A cm^{-2} @ 1.76 V and 80°C and 2 A cm^{-2} @ 2V @ 80°C [60]. The application of the same material to the electrochemical reforming of ethanol delivering 2 A cm^{-2} @ 0.9 V @ 80°C[60]. A Pd/TNTA anode in alkaline direct ethanol fuel cells produced a power density exceeding 300 mW cm^{-2}, one of the highest value reported so far. [61]

Conclusions and perspectives

In this short review, we have discussed some of the most relevant recent application of titanium dioxide as a support material for electrocatalysis. These applications have shown that the use of titania in electrocatalysis leads to substantial advantages over the conventional high surface area carbon supports. These advantages include higher stability, synergistic effects with better energetics and the possibility of facile synthesis to obtain embedded nanostructures with mechanical stability over large surface areas. We believe that this last point deserves much attention as it may lead to a new paradigm to realize catalytic layers that do not include nanomaterials that can be released into the environment or be potentially hazardous for workers. However, to fully understand the potential of titania in electrocatalysis and particularly of the most recent self-standing nanostructures, much research is still needed (Table 2). We believe that titania nanostructure and especially the recent 3D TNTA may contribute much to boost the performance of the following applications: i) alkaline membrane electrolysis, ii) direct liquid fuel cells, iii) electrochemical reformers, iv) CO_2 electroreduction and v) the electrochemical fixation of nitrogen [62].

Table 2 - the research needs to make titania progress in electrocatalysis, together with the potential target to achieve

Research Action	Expected outcome	Target
Assessing long term stability and understanding the degradation mechanism	- Define the duration of TiO_2 catalysts based on recognized protocols for each application - Understand the cause of degradation and design mitigation strategies	- Provide an accurate benchmarking with the state-of-the-art - Delivering more corrosion resistant materials (e.g. by doping with other metals)
Moving from powders to embedded titania nanomaterials	- Reduce the potential health and environmental risk of nanomaterials	- Zero risk of nanomaterials release into the environment - Zero risk of nanomaterials contamination in the workplace
Realization of thin nanomaterials structure with embedded titania nanostructures	- Carbon-free titania supported catalytic layers with a thickness comparable to the catalyst layer of state-of-the-art PEMFCs	- Delivery of catalytic layers based on embedded or powder nanostructures that work in gas-fed fuel cells and electrolytic devices (thickness less than 25 µm)
Functionalization of titania surfaces to provide surface ionic conductivity in embedded nanostructures	- Ionic conductivity of ionomer-free catalytic layer comparable to that of current carbon-based technologies	- MEAs for fuel cells and electrolyzers with Area Specific resistance of less than 0.07 ohm cm^{-2}
Functionalization of titania surfaces for single site electrocatalysis	- Molecular or organometallic compounds acting as single site electrocatalysts	- Application of the electrodes in fuel cells and electrolysis outperforming carbon supported single site catalysts
Extensive testing of embedded in direct liquid fuel cells	- Embedded architectures optimized for the use in direct liquid fuel cells	- Beyond 0.5 W cm^{-2} in direct ethanol fuel cells and C3-C4 alcohols fuel cells
Extensive testing of titania nanomaterials in electrolytic devices	- Assessing the performance of embedded and non-embedded titania-based electrodes in alkaline electrolysis, CO_2RR and nitrogen fixation	- 2 A cm^{-2} @1.8 V in alkaline membrane water electrolyzers. - Benchmarking of the novel electrode architectures with the state of the art for CO_2RR and nitrogen fixation

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References

[1] A. FUJISHIMA, K. HONDA, Electrochemical Photolysis of Water at a Semiconductor Electrode, Nature. 238 (1972) 37–38. doi:10.1038/238037a0.

[2] J. Schneider, M. Matsuoka, M. Takeuchi, J. Zhang, Y. Horiuchi, M. Anpo, D.W. Bahnemann, Understanding TiO 2 Photocatalysis: Mechanisms and Materials, Chem. Rev. 114 (2014) 9919–9986. doi:10.1021/cr5001892.

[3] S.N.A. Shah, Z. Shah, M. Hussain, M. Khan, Hazardous Effects of Titanium Dioxide Nanoparticles in Ecosystem, Bioinorg. Chem. Appl. 2017 (2017) 1–12. doi:10.1155/2017/4101735.

[4] Y. Pan, M. Tu, X. Shi, Q. Zhang, X. Guo, M. Li, Y. Wu, Y. Ying, Y. Wen, H. Yang, Metal-Support Synergetic Effect for Elevating PtPd Electrocatalytic Performance, J. Electrochem. Soc. 166 (2019) F264–F269. doi:10.1149/2.0871904jes.

[5] Y. Ma, X. Wang, Y. Jia, X. Chen, H. Han, C. Li, Titanium Dioxide-Based Nanomaterials for Photocatalytic Fuel Generations, Chem. Rev. 114 (2014) 9987–10043. doi:10.1021/cr500008u.

[6] S. Sharma, B.G. Pollet, Support materials for PEMFC and DMFC electrocatalysts—A review, J. Power Sources. 208 (2012) 96–119. doi:10.1016/j.jpowsour.2012.02.011.

[7] T. Ioroi, T. Akita, S. Yamazaki, Z. Siroma, N. Fujiwara, K. Yasuda, Corrosion-Resistant PEMFC Cathode Catalysts Based on a Magnéli-Phase Titanium Oxide Support Synthesized by Pulsed UV Laser Irradiation, J. Electrochem. Soc. 158 (2011) C329. doi:10.1149/1.3622297.

[8] I. Savych, J. Bernard d'Arbigny, S. Subianto, S. Cavaliere, D.J. Jones, J. Rozière, On the effect of non-carbon nanostructured supports on the stability of Pt nanoparticles during voltage cycling: A study of TiO2 nanofibres, J. Power Sources. 257 (2014) 147–155. doi:10.1016/j.jpowsour.2014.01.112.

[9] M. Kim, C. Kwon, K. Eom, J. Kim, E. Cho, Electrospun Nb-doped TiO2 nanofiber support for Pt nanoparticles with high electrocatalytic activity and durability, Sci. Rep. 7 (2017) 44411. doi:10.1038/srep44411.

[10] O. Lori, L. Elbaz, Advances in Ceramic Supports for Polymer Electrolyte Fuel Cells, Catalysts. 5 (2015) 1445–1464. doi:10.3390/catal5031445.

[11] S. Shanmugam, A. Gedanken, Synthesis and Electrochemical Oxygen Reduction of Platinum Nanoparticles Supported on Mesoporous TiO 2, J. Phys. Chem. C. 113 (2009) 18707–18712. doi:10.1021/jp908322h.

[12] N. Abdullah, S.K. Kamarudin, Titanium dioxide in fuel cell technology: An overview, J. Power Sources. 278 (2015) 109–118. doi:10.1016/j.jpowsour.2014.12.014.

[13] Z. Weng, H. Guo, X. Liu, S. Wu, K.W.K. Yeung, P.K. Chu, Nanostructured TiO2 for energy conversion and storage, RSC Adv. 3 (2013) 24758. doi:10.1039/c3ra44031a.

[14] (●●) T.N. Geppert, M. Bosund, M. Putkonen, B.M. Stühmeier, T. Pasanen, P. Heikkilä, H.A. Gasteiger, H.A. El-sayed, HOR Activity of Pt-TiO 2-Y at Unconventionally High Potentials Explained : The Influence of SMSI on the Electrochemical Behavior of Pt HOR Activity of Pt-TiO 2-Y at Unconventionally High Potentials Explained : The In fl uence of SMSI on the Electrochemica, (2020). doi:10.1149/1945-7111/ab90ae.

A deep analysis of the synergistic effects between titanium diioxde and metal in electrocatalysis with evidence of hydrogen and oxygen through TiO2 thin films on Pt nanoparticles

[15] S. Donthu, M. Cai, M. Ruthkosky, I. Halalay, Carbon–titania composite substrates for fuel cell catalyst applications, Chem. Commun. (2009) 4203. doi:10.1039/b906265c.

[16] (●) H. Uzal, A. Döner, Corrosion Behavior of Titanium Dioxide Nanotubes in Alkaline Solution, 56 (2020) 311–319. doi:10.1134/S207020512002029X.

One of the few investigation of titania nanotube corrosion that investigates degradation with a focus on alkaline electrolytes

[17] M.T. Anwar, X. Yan, S. Shen, N. Husnain, F. Zhu, L. Luo, J. Zhang, Enhanced durability of Pt electrocatalyst with tantalum doped titania as catalyst support, Int. J. Hydrogen Energy. 42 (2017) 30750–30759. doi:10.1016/j.ijhydene.2017.10.152.

[18] G. Cabello, R.A. Davoglio, E.C. Pereira, Microwave-assisted synthesis of anatase-TiO 2 nanoparticles with catalytic activity in oxygen reduction, J. Electroanal. Chem. 794 (2017) 36–42. doi:10.1016/j.jelechem.2017.04.004.

[19] M.M. Mohamed, M. Khairy, S. Eid, Activity and stability studies of titanates and titanate-carbon nanotubes supported Ag anode catalysts for direct methanol fuel cell, J. Power Sources. 304 (2016) 255–265. doi:10.1016/j.jpowsour.2015.11.054.

[20] (●) B. Ren, Q. Jin, Y. Li, Y. Li, H. Cui, C. Wang, Activating Titanium Dioxide as a New Efficient Electrocatalyst: From Theory to Experiment, ACS Appl. Mater. Interfaces. 12 (2020) 11607–11615. doi:10.1021/acsami.9b21575.

Cu doping boosts titania activity toward the HER. Cu can strengthen the orbital hybridization of H1s and O2p favoring the hydrogen adsorption/desorption and improving electrical conductivity

[21] A. Lavacchi, H. Miller, F. Vizza, Nanotechnology in Electrocatalysis for Energy, Springer New York, New York, NY, 2013. doi:10.1007/978-1-4899-8059-5.

[22] M. Yuan, Y. Zhu, L. Deng, R. Ming, A. Zhang, W. Li, B. Chai, Z. Ren, IrO 2 –TiO 2 electrocatalysts for the hydrogen evolution reaction in acidic water electrolysis without activation, New J. Chem. 41 (2017) 6152–6159. doi:10.1039/C7NJ00756F.

[23] F. Yang, L. Ma, M. Gan, J. Zhang, J. Yan, H. Huang, L. Yu, Y. Li, C. Ge, H. Hu, Polyaniline-functionalized TiO2–C supported Pt catalyst for methanol electro-oxidation, Synth. Met. 205 (2015) 23–31. doi:10.1016/j.synthmet.2015.03.017.

[24] (●●) M. Eckardt, C. Gebauer, Z. Jusys, M. Wassner, N. Hüsing, R.J. Behm, Oxygen reduction reaction activity and long-term stability of platinum nanoparticles supported on titania and titania-carbon nanotube composites, J. Power Sources. 400 (2018) 580–591. doi:10.1016/j.jpowsour.2018.08.036.

An analysis of the activity and stability of fuel cell cathodes that include TiO2 nanomaterials. The paper shows that titania degradation mainly occurs under reductive treatments in the course of accelerated degradation tests.

[25] (●) E.C.M. Barbosa, L.S. Parreira, I.C. de Freitas, L.R. Aveiro, D.C. de Oliveira, M.C. dos Santos, P.H.C. Camargo, Pt-Decorated TiO 2 Materials Supported on Carbon: Increasing Activities and Stabilities toward the ORR by Tuning the Pt Loading, ACS Appl. Energy Mater. 2 (2019) 5759–5768. doi:10.1021/acsaem.9b00879.

An exploration of the Pt loading on the stability of fuel cell electrode loaded with nanostructured titania

[26] J. Zhang, X. Hu, F. Zhu, N. Su, H. Huang, J. Cheng, H. Yang, Simple synthesized Pt/GNs/TiO 2 with good mass activity and stability for methanol oxidation, Nanotechnology. 28 (2017) 505603. doi:10.1088/1361-6528/aa9699.

[27] W.-T. Chiu, Y.-H. Chiu, P.-Y. Hsieh, T.-F.M. Chang, M. Sone, Y.-J. Hsu, A. Tixier-Mita, H. Toshiyoshi, Nano-Au Catalysts Modified with TiO 2 : Enhancement of Electrocatalytic Activity for 1-Propanol

Oxidation in Alkaline Media, J. Electrochem. Soc. 166 (2019) F760–F767. doi:10.1149/2.0741912jes.

[28] A. Fraser, Z. Zhang, G. Merle, U. Gbureck, S. Ye, J. Gostick, J. Barralet, Composite Carbon Nanotube Microsphere Coatings for Use as Electrode Supports, Adv. Funct. Mater. 28 (2018) 1803713. doi:10.1002/adfm.201803713.

[29] J. Li, L. Zhao, X. Li, S. Hao, Z. Wang, Carbon-Coated and Interfacial-Functionalized Mixed-Phase Mo x Ti 1− x O 2-δ Nanotubes as Highly Active and Durable PtRu Catalyst Support for Methanol Electrooxidation, Chem. – An Asian J. 14 (2019) 1549–1556. doi:10.1002/asia.201900264.

[30] M. Chen, M. Wang, Z. Yang, X. Wang, High performance and durability of order-structured cathode catalyst layer based on TiO 2 @PANI core-shell nanowire arrays, Appl. Surf. Sci. 406 (2017) 69–76. doi:10.1016/j.apsusc.2017.01.296.

[31] M. Liu, M. Zhou, H. Yang, G. Ren, Y. Zhao, Titanium dioxide nanoparticles modified three dimensional ordered macroporous carbon for improved energy output in microbial fuel cells, Electrochim. Acta. 190 (2016) 463–470. doi:10.1016/j.electacta.2015.12.131.

[32] S. Hussain, H. Erikson, N. Kongi, A. Tarre, P. Ritslaid, M. Rähn, L. Matisen, M. Merisalu, V. Sammelselg, K. Tammeveski, Pt nanoparticles sputter-deposited on TiO2/MWCNT composites prepared by atomic layer deposition: Improved electrocatalytic activity towards the oxygen reduction reaction and durability in acid media, Int. J. Hydrogen Energy. 43 (2018) 4967–4977. doi:10.1016/j.ijhydene.2018.01.143.

[33] M. Soleimani-Lashkenari, S. Rezaei, J. Fallah, H. Rostami, Electrocatalytic performance of Pd/PANI/TiO 2 nanocomposites for methanol electrooxidation in alkaline media, Synth. Met. 235 (2018) 71–79. doi:10.1016/j.synthmet.2017.12.001.

[34] S. Roy, S. Payra, S. Challagulla, R. Arora, S. Roy, C. Chakraborty, Enhanced Photoinduced Electrocatalytic Oxidation of Methanol Using Pt Nanoparticle-Decorated TiO 2 –Polyaniline Ternary Nanofibers, ACS Omega. 3 (2018) 17778–17788. doi:10.1021/acsomega.8b02610.

[35] M. Marszewski, S. Cao, J. Yu, M. Jaroniec, Semiconductor-based photocatalytic CO 2 conversion, Mater. Horizons. 2 (2015) 261–278. doi:10.1039/C4MH00176A.

[36] M. Aresta, A. Dibenedetto, A. Angelini, Catalysis for the Valorization of Exhaust Carbon: from CO 2 to Chemicals, Materials, and Fuels. Technological Use of CO 2, Chem. Rev. 114 (2014) 1709–1742. doi:10.1021/cr4002758.

[37] L. Zhang, Z.-J. Zhao, J. Gong, Nanostructured Materials for Heterogeneous Electrocatalytic CO 2 Reduction and their Related Reaction Mechanisms, Angew. Chemie Int. Ed. 56 (2017) 11326–11353. doi:10.1002/anie.201612214.

[38] (●) M.A. Farkhondehfal, S. Hernández, M. Rattalino, M. Makkee, A. Lamberti, A. Chiodoni, K. Bejtka, A. Sacco, F.C. Pirri, N. Russo, Syngas production by electrocatalytic reduction of CO2 using Ag-decorated TiO2 nanotubes, Int. J. Hydrogen Energy. (2019). doi:10.1016/j.ijhydene.2019.04.180.

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[39] P.P. Sharma, F.-S. Ke, X.-D. Zhou, The Role of Nonstoichiometry on the Electrocatalytic Properties of TiO2- towards the Conversion of Carbon Dioxide to Fuels, ECS Trans. 61 (2014) 331–339. doi:10.1149/06101.0331ecst.

[40] J.-X. Feng, H. Xu, Y.-T. Dong, X.-F. Lu, Y.-X. Tong, G.-R. Li, Efficient Hydrogen Evolution Electrocatalysis Using Cobalt Nanotubes Decorated with Titanium Dioxide Nanodots, Angew. Chemie Int. Ed. 56 (2017) 2960–2964. doi:10.1002/anie.201611767.

[41] (●) B. Feng, C. Liu, W. Yan, J. Geng, G. Wang, MoS 2 nanotubes loaded with TiO 2 nanoparticles for enhanced electrocatalytic hydrogen evolution, RSC Adv. 9 (2019) 26487–26494. doi:10.1039/C9RA05041H.

The application of nanostructured titania to create synergistic structure with MoS_2 *to provide efficient HER.*

[42] V. Zwilling, E. Darque-Ceretti, A. Boutry-Forveille, D. David, M.Y. Perrin, M. Aucouturier, Structure and physicochemistry of anodic oxide films on titanium and TA6V alloy, Surf. Interface Anal. 27 (1999) 629–637. doi:10.1002/(SICI)1096-9918(199907)27:7<629::AID-SIA551>3.0.CO;2-0.

[43] V. Zwilling, M. Aucouturier, E. Darque-Ceretti, Anodic oxidation of titanium and TA6V alloy in chromic media. An electrochemical approach, Electrochim. Acta. 45 (1999) 921–929. doi:10.1016/S0013-4686(99)00283-2.

[44] D. Gong, C.A. Grimes, O.K. Varghese, W. Hu, R.S. Singh, Z. Chen, E.C. Dickey, Titanium oxide nanotube arrays prepared by anodic oxidation, J. Mater. Res. 16 (2001) 3331–3334. doi:10.1557/JMR.2001.0457.

[45] R. Beranek, H. Hildebrand, P. Schmuki, Self-Organized Porous Titanium Oxide Prepared in H[sub 2]SO[sub 4]/HF Electrolytes, Electrochem. Solid-State Lett. 6 (2003) B12. doi:10.1149/1.1545192.

[46] J.M. Macak, K. Sirotna, P. Schmuki, Self-organized porous titanium oxide prepared in Na2SO4/NaF electrolytes, Electrochim. Acta. 50 (2005) 3679–3684. doi:10.1016/j.electacta.2005.01.014.

[47] J.M. Macák, H. Tsuchiya, P. Schmuki, High-Aspect-Ratio TiO 2 Nanotubes by Anodization of Titanium, Angew. Chemie Int. Ed. 44 (2005) 2100–2102. doi:10.1002/anie.200462459.

[48] L. V. Taveira, J.M. Macák, H. Tsuchiya, L.F.P. Dick, P. Schmuki, Initiation and Growth of Self-Organized TiO[sub 2] Nanotubes Anodically Formed in NH[sub 4]F⁄(NH[sub 4])[sub 2]SO[sub 4] Electrolytes, J. Electrochem. Soc. 152 (2005) B405. doi:10.1149/1.2008980.

[49] A. Ghicov, H. Tsuchiya, J.M. Macak, P. Schmuki, Titanium oxide nanotubes prepared in phosphate electrolytes, Electrochem. Commun. 7 (2005) 505–509. doi:10.1016/j.elecom.2005.03.007.

[50] J. Ni, K. Noh, C.J. Frandsen, S.D. Kong, G. He, T. Tang, S. Jin, Preparation of near micrometer-sized TiO2 nanotube arrays by high voltage anodization, Mater. Sci. Eng. C. 33 (2013) 259–264. doi:10.1016/j.msec.2012.08.038.

[51] J.M. Macak, S.P. Albu, P. Schmuki, Towards ideal hexagonal self-ordering of TiO2 nanotubes, Phys. Status Solidi – Rapid Res. Lett. 1 (2007) 181–183. doi:10.1002/pssr.200701148.

[52] H. Tsuchiya, J.M. Macak, L. Taveira, E. Balaur, A. Ghicov, K. Sirotna, P. Schmuki, Self-organized TiO2 nanotubes prepared in ammonium fluoride containing acetic acid electrolytes, Electrochem. Commun. 7 (2005) 576–580. doi:10.1016/j.elecom.2005.04.008.

[53] P. Roy, S. Berger, P. Schmuki, TiO2 Nanotubes: Synthesis and Applications, Angew. Chemie Int. Ed. 50 (2011) 2904–2939. doi:10.1002/anie.201001374.

[54] S. Bauer, S. Kleber, P. Schmuki, TiO2 nanotubes: Tailoring the geometry in H3PO4/HF electrolytes, Electrochem. Commun. 8 (2006) 1321–1325. doi:10.1016/j.elecom.2006.05.030.

[55] Y.-X. Chen, T. Jacob, Function Calculation: A Simple Way to Predict the Geometry Parameters of Self-Organized Titania Nanotube Arrays, ChemElectroChem. 4 (2017) 476–480. doi:10.1002/celc.201600860.

[56] Y.-X. Chen, A. Lavacchi, S.-P. Chen, F. di Benedetto, M. Bevilacqua, C. Bianchini, P. Fornasiero, M. Innocenti, M. Marelli, W. Oberhauser, S.-G. Sun, F. Vizza, Electrochemical Milling and Faceting: Size Reduction and Catalytic Activation of Palladium Nanoparticles, Angew. Chemie Int. Ed. 51 (2012)

8500–8504. doi:10.1002/anie.201203589.

[57] M. Wang, D. Guo, H. Li, High activity of novel Pd/TiO2 nanotube catalysts for methanol electro-oxidation, J. Solid State Chem. 178 (2005) 1996–2000. doi:10.1016/j.jssc.2005.04.006.

[58] M. Bevilacqua, C. Bianchini, A. Marchionni, J. Filippi, A. Lavacchi, H. Miller, W. Oberhauser, F. Vizza, G. Granozzi, L. Artiglia, S.P. Annen, F. Krumeich, H. Grützmacher, Improvement in the efficiency of an OrganoMetallic Fuel Cell by tuning the molecular architecture of the anode electrocatalyst and the nature of the carbon support, Energy Environ. Sci. 5 (2012) 8608. doi:10.1039/c2ee22055e.

[59] S.P. Annen, V. Bambagioni, M. Bevilacqua, J. Filippi, A. Marchionni, W. Oberhauser, H. Schönberg, F. Vizza, C. Bianchini, H. Grützmacher, A Biologically Inspired Organometallic Fuel Cell (OMFC) That Converts Renewable Alcohols into Energy and Chemicals, Angew. Chemie Int. Ed. 49 (2010) 7229–7233. doi:10.1002/anie.201002234.

[60] Y.X. Chen, A. Lavacchi, H.A. Miller, M. Bevilacqua, J. Filippi, M. Innocenti, A. Marchionni, W. Oberhauser, L. Wang, F. Vizza, Nanotechnology makes biomass electrolysis more energy efficient than water electrolysis, Nat. Commun. 5 (2014) 4036. doi:10.1038/ncomms5036.

[61] Y. Chen, M. Bellini, M. Bevilacqua, P. Fornasiero, A. Lavacchi, H.A. Miller, L. Wang, F. Vizza, Direct Alcohol Fuel Cells: Toward the Power Densities of Hydrogen-Fed Proton Exchange Membrane Fuel Cells, ChemSusChem. 8 (2015) 524–533. doi:10.1002/cssc.201402999.

[62] Y.-H. Liu, M.H. Vu, J. Lim, T.-O. Do, M.C. Hatzell, Influence of carbonaceous species on aqueous photo-catalytic nitrogen fixation by titania, Faraday Discuss. 215 (2019) 379–392. doi:10.1039/C8FD00191J.

Declaration of interests

☒ 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.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: