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Trend in using TiO2 nanotubes as photoelectrodes in PEC processes for wastewater treatment

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Abstract - Photoelectrochemical (PEC) processes represent an effective way to exploit renewable energy in response to the sustainable development objectives. The synergy between photo and electrochemical processes inspired several papers and stimulated research toward new systems that could be increasingly adapted to work under visible or solar radiation, and with minimum bias potential. Since the first appearance of articles on PEC processes in the literature, titanium dioxide has been one of the most studied semiconductor materials: nanostructured electrodes have been especially considered such as nanotubes (NT), which are the main subject of the present article. The software VOSviewer is used to a preliminary analysis of metadata, related to the trend of the research on PEC processes; attention is then paid on the trend of NT-TiO2 electrodes for application in wastewater treatment in the past year.

Introduction

With the advent of green electricity production, electrochemical technologies gained in importance. Hybrid processes are now very commonly considered, in which an electrochemical stage is combined with chemical, physical or biological stages. A typical example is represented by photoelectrocatalytic (PEC) processes in which electrochemical (EC) and photochemical (PC) processes are combined: the synergy of the two processes can be seen both from the point of view of the PC process, which increases its efficiency as the bias potential lowers recombination of the photogenerated charges, but also from the EC point, as the photo-potential generated on the semiconductor, allows depolarizing the cell, thus lowering the costs of the whole process [1].

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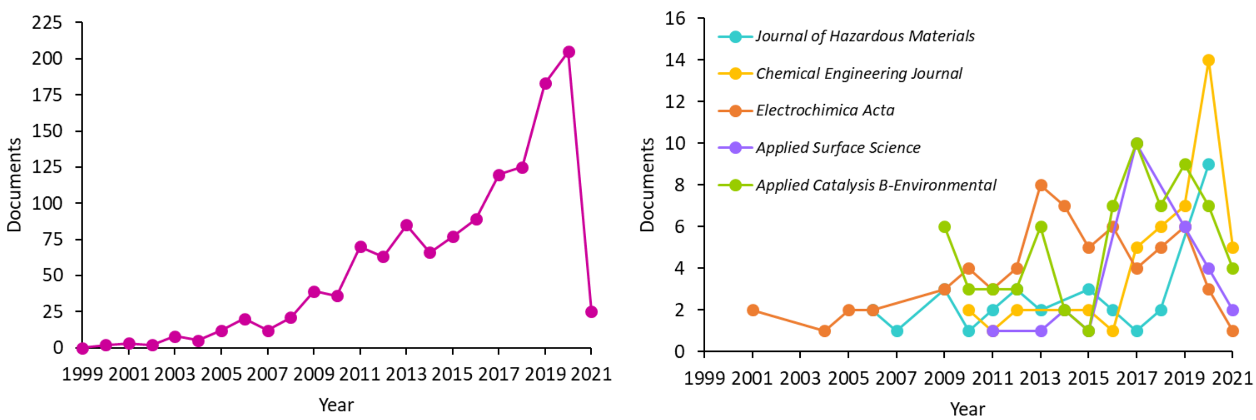
Above all, PEC processes have become an attractive strategy for wastewater treatment and simultaneous H2 production [2–5].

In this article attention has been paid on the recent literature to verify the research progress on one of the most used electrode materials, TiO2 nanotubes (NT), and to verify if it is still appealing for PEC wastewater treatment processes. The discussion on these data, will be preceded by a brief analysis of metadata related to PEC processes.

Metadata analysis on Photoelectrocatalysis

Starting from bibliographic data available on SCOPUS, which allowed a preliminary numerical analysis, data have been elaborated by the software VOSviewer[2], an effective visualization tool developed by Eck and Waltman [6] which can be used to cluster publications and to obtain a comprehensive overview of the results. Records from SCOPUS included data of publication year, author, institution, and source journal, as well as data related to the documents, such as keywords (kwds), titles, and abstracts. Simply typing the kwd "Photoelectrocatalysis", without any time limit, 1288 documents were extracted, from which the beginning of the research on this technology can be traced back to 2001 (see figure1). Articles were initially published only on *Electrochimica Acta*, then in the last 10 years, other sources were also involved. Particularly noteworthy is, in the last 10 years, the surge in articles on *Hazardous Materials* and *Chemical Engineering Journal*, and the decrease of papers on *Electrochimica Acta* which could indicate that the technology is moving from the fundamentals to real applications.



[2]VOSviewer-version 1.6.16 https://www.vosviewer.com/

Figure 1 - Trend of the number of documents per year (a) and documents per year by source for the top five sources ordered by number of documents (b), found searching “photoelectrocatalysis” in SCOPUS.

The records were then imported on VOSviewer and subjected to a first **Co-authorship analysis,** which allows evaluating the original countries of the authors of the selected works, and the possible collaboration between them. Scientific articles are considered, whereas reviews are excluded from the following analysis. The map of the result is shown in Figure 2:

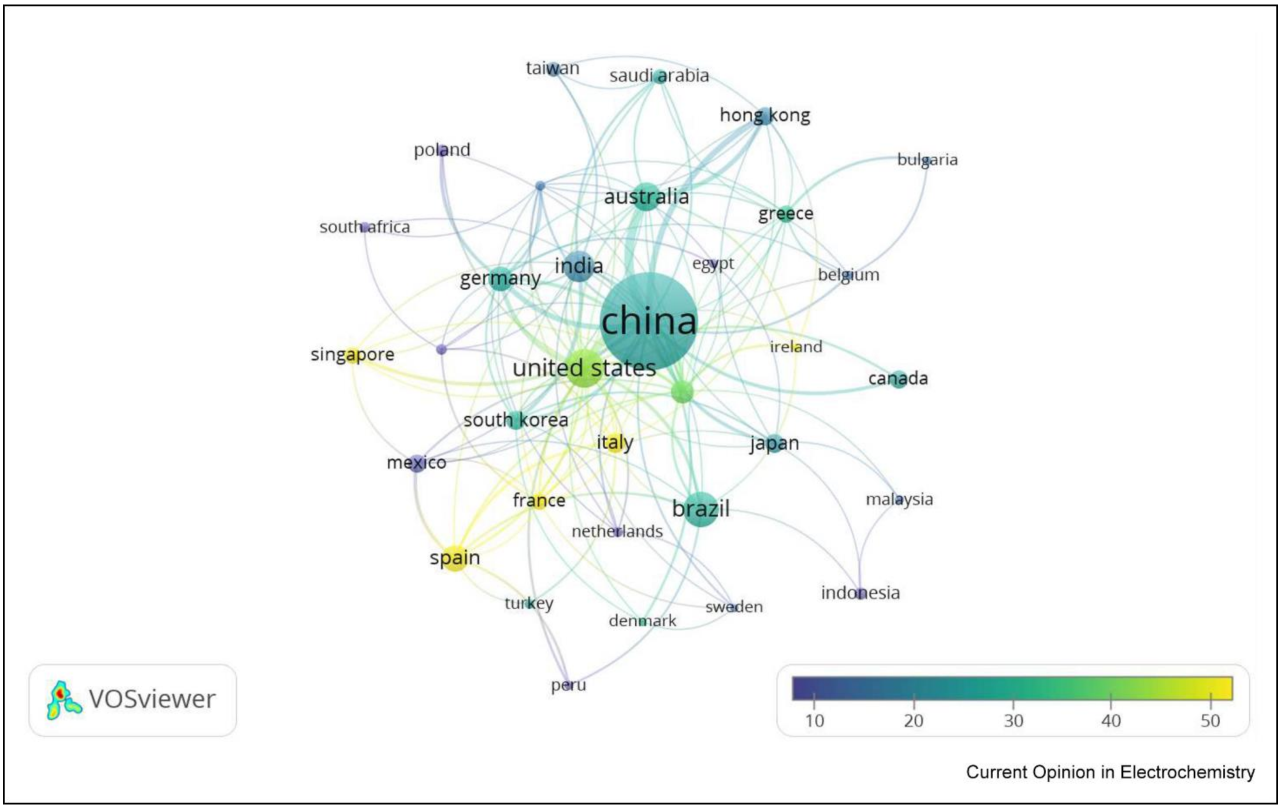


Figure 2 - Co-authorship analysis: Visualization map of countries participating in research involving photoelectrocatalysis. Colors in the map are based on the average citations of articles from the country (evaluated as total citation/total articles). An interactive visualization of the map is available at http://bit.ly/35RWQr0 [3]

Dimension of the dots depends on the number of documents published by authors belonging to the related country. Links between items indicate the relatedness between the countries, which is determined based on the number of co-authored documents.

Among the 62 countries involved, the map represents the 35 of them which have had at least 5 published articles. The highest number of papers is related to China (636 documents with 22 co-authorship links), followed by the United State and Brazil with 99 and 33 documents, co-authored

[3] The installation of Java 1.8.0 is needed before copying the link on the browser.

with 24 and 10 countries, respectively. Colors in the map are also indicative of citation: in the above visualization data are weighted by the average number of citations that total papers of a country received. Spain, France, Italy and Singapore are among the countries that produced works with the highest average number of citations.

Figure 3 presents the result of the **Co-occurence** analysis:

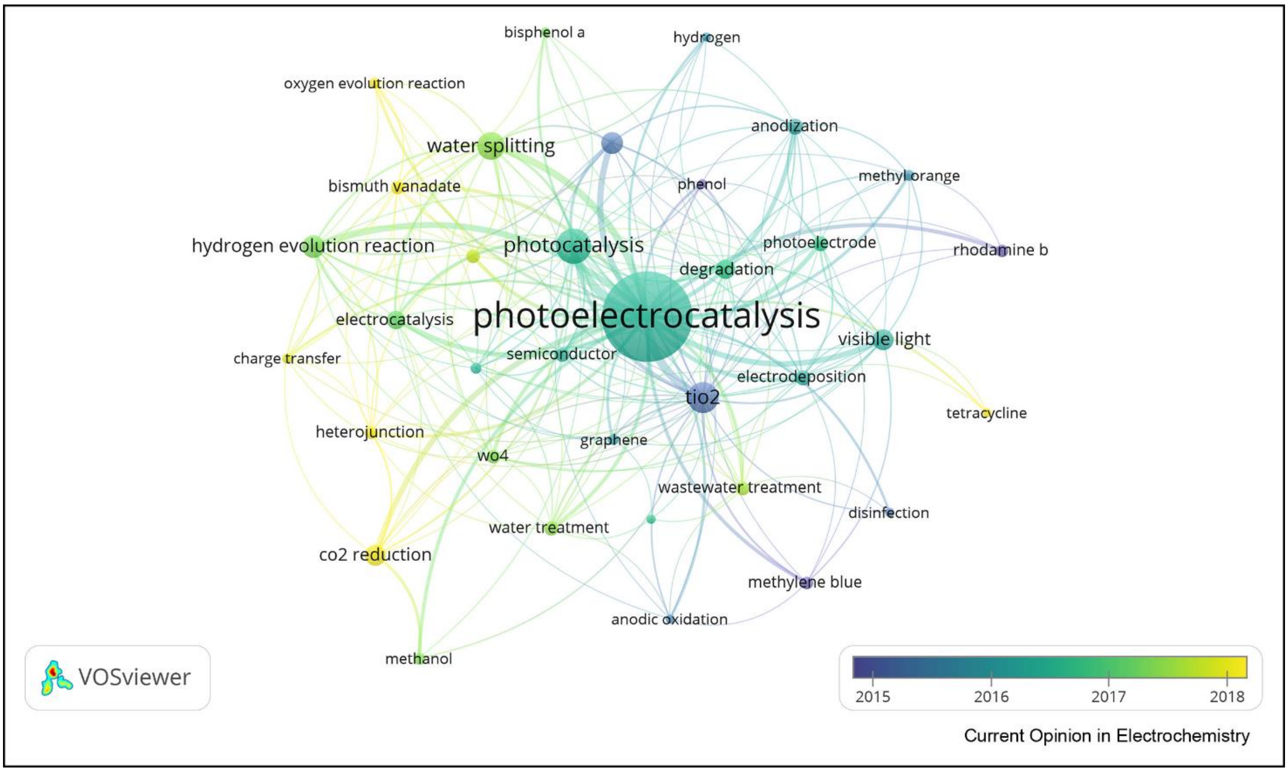


Figure 3- Co-occurrence analysis: Visualization map of keywords in articles involving photoelectrocatalysis. Colors in the map are based on the average year of publication of the articles that report the related kwds. An interactive visualization of the map is available at http://bit.ly/3sxFj0W [4]

In this case the items represent the kwds provided in the selected articles. More than 2000 kwds have been identified. Among them 31 kwds were selected as the most influential ones, which were repeated at least 10 times in the whole mass of the articles. The dot size varies depending on the occurrence (ocr) of the kwd; the links between kwds indicate a relatedness, based on the number of documents in which they occur together: the higher this number, the thicker the link. Colors give indication on the topics which are more currently under study: a score is attributed to the items, evaluated as the average year of publication of the articles that report the related kwds. If size of the items is compared, high relevance assume terms such as *photocatalysis* (ocr = 120), as the photocatalytic performances are very often

[4] The installation of Java 1.8.0 is needed before copying the link on the browser.

compared with those of PEC processes; then TiO2 (ocr = 95) the most investigated semiconductor, and *TiO2 NT* (ocr = 47), which represents the most studied morphology. The weight of these items is around the value of 2015 (purple colored in the map) to indicate the average date of articles on these topics.

Looking at the data more specifically, we note that, along with *CO2 reduction* (ocr = 44, weight around 2018, yellow in the map), one of the sectors in which application of PEC is more recently addressed is *water splitting* (ocr = 72, weight 2017), which is also evidenced by the item *Hydrogen evolution reaction* (ocr = 48). As it could be expected, the production of green H2 is becoming an absolute priority, from an environmentally sustainable point of view. However, also PEC applications to *wastewater* (ocr = 18) and *water treatment* (ocr = 22), may be enclosed in the actual trend of articles aimed at PEC oxidation of biorefractory compounds, in which oxidation of organics may be combined with the H2 evolution at the cathode.

TiO2 Nanotubes: use in PEC processes

As indicated by the previous analysis, TiO2 is one of the most studied materials for PEC processes, which has been proposed in different highly porous nanostructures, and morphologies. As in all heterogeneous EC processes, high surface area of the electrode is one of the fundamental requirements to favor the electron transfer on specific active sites at the electrode surface.

Among the various TiO2 structures, NT always aroused great interest. Especially when the NT are obtained directly by oxidation of titanium sheet, the resulting structure presents numerous advantages: supported catalysts avoid separation and recovery of the catalyst at the end of the process; NT are oriented perpendicular to the substrate surface, thus maintaining mechanical and electrical contact with the substrate, which represents another important point for the success of PEC catalysts [7].

The analysis of SCOPUS data (figure 4) indicated that in the last 5 years the average number of articles is always greater than 800 / year and about half of them are dedicated to application of NT in PEC processes. The figure below also shows the share of PEC articles per year involving specific applications.

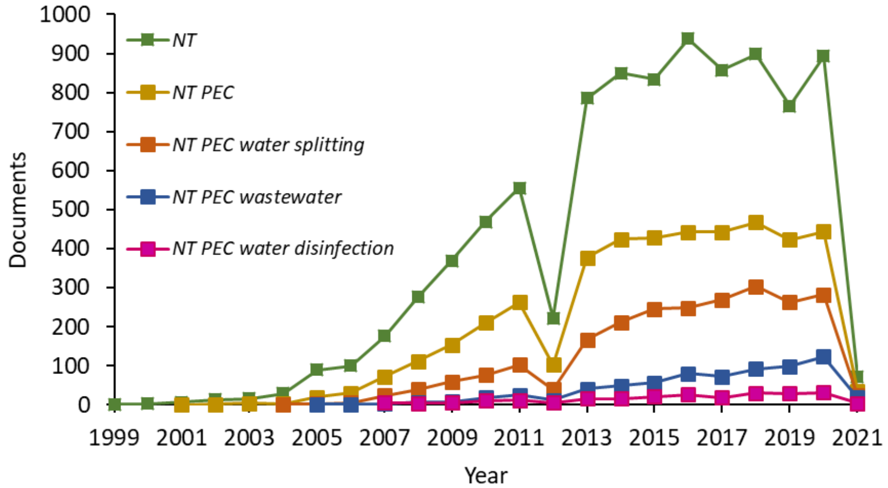


Figure 4- Annual trend of the number of articles on TiO2-NT (green);TiO2-NT and PEC (yellow); TiO2-NT and PEC and water splitting (red); TiO2-NT and PEC and wastewater treatment (blue); TiO2-NT and PEC and water disinfection (pink).

In the following, a more detailed analysis is presented on specific aspects studied by the different articles which appeared in the literature, during the past year 2020, along with those already published in 2021. We noticed that only in rare cases, NT are proposed as such [8-11]. Most of the studies are mainly dedicated to understanding the operating mechanism of the structure and investigating the synthesis operating conditions to improve its performance [10,12-14] or to increase its stability to corrosion [15]. As it is well known, the used synthesis technique of the electrodes affects both the final morphology of the structure, and the distribution of active sites and defects, which play a key role on the light absorption, and in turn on the PEC performance of the final sample [16,17].

Most of the works concern with structures in which TiO2 NT are modified: the immobilization of metals / non-metals [18-19] as dopants, combination with inert layers like graphene oxide, graphitic carbon nitride or carbon NTs [20-23], noble metal [24-25], as well as with other oxides [26-27] and sulphides [28-29] , and functionalization with polymers [30] or visible light sensitizing [31], have been proposed to enhance the response to wider range of wavelengths.

If we analyze the applications proposed for these kinds of structures, the following subtopics can be individuated inside the general topic of PEC wastewater treatment.

- AOP of biorefractory compounds [18, 27, 32]
- Degradation of organic microcontaminants (OMCs) and inactivation of bacteria [26-33]
- Removal of toxic metallic compounds such as Cr (VI) [34]

- Degradation of drugs [23-25, 35-38], dyes [39-42], and volatile organic compounds [27].

Final considerations and future perspectives

From the analysis above reported it's clear that research on NT in PEC process is still very active. NT may be seen as a valid alternative to the bulk catalysts commonly used in PC process: in that case the bulk electrodes constructed by coating powdered catalysts on conductive glass, caused decrease in mass transfer rate and dispersion of the catalyst at the end of the process. NT structures may contribute solving these problems. Many attempts are still devoted to find new routes of their synthesis, and to identify particular structural changes that allow decreasing costs, increasing the lifetime [23] and performance [43] of the electrodes so they can be competitive with respect to those generally proposed in EAOP [19] such as BDD, PbO_2, DSA and Pt anodes. An interesting article reports the results of a particular procedure to obtain NT powders starting from wastewater discharged from the nitrogen thermal plasma decomposition of refrigerants. The waste solution was reused to obtain high value-added TiO_2 nanopowders: owing to a weak adhesiveness between oxide and substrate, the nanotubes spontaneously detached from the substrate during anodization. Authors expect this process being applicable at an industrial scale [44]*. NT are also proposed in solar multifield-driven hybrid chemical system for purification of organic in wastewater [45]*: nano-carbon/TiO_2/Ti obtained by deposition of carbon NT onto TiO_2 NT gave good mineralization of nitrobenzene, via multifield-driven thermo-photo-electrochemistry. The results indicated that the three-field pattern system achieved greater oxidation efficiency compared to the one- or two-field patterns.

The proposal of using NT in microreactors is also of great interest [46]*. The possibility of separating the reaction products in different channels may open new ways for application of these devices also for water splitting in which H_2 and O_2 have to be kept separated. Parallelly, we also assist to another direction of the research, towards the development and improvement of the unbiased self-driving photoelectrocatalytic reactors [47]**: a self-driven double-side illumination photo-electrocatalytic reactor was designed for simultaneous PEC H_2 evolution on the photocathode (Pt cluster modified Si-nanowires) and organic pollutants degradation on TiO_2 NT photoanode.

A consideration can be made downstream of the analysis presented previously, regarding the fact that, if we exclude the work of Rajput [48]* which proposes Au / TiO_2NT for the treatment of wastewater from the pulp and paper industry and extend the results on a pilot plant, most of the articles deal with laboratory-scale processes. There are not many proposals for applications on a large scale and real systems.

The non-selectivity of the PEC process can be one of the reasons of this fact. Along with the organic compound of interest, real wastewater may also contain other organic/inorganic species which may have competition and/or inhibition effects, as well as electrode fouling problems. Natural organic matter may be present, which may be harmless to human health and may not need removal to a trace level. However, they can compete at active sites of the catalyst, so reducing the performance in the removal of the toxic compound. The combination of TiO2 NT with SiO2 with controlled porosity, is proposed [49]** to create a system that simultaneously filters and treats phthalates contained in a solution in which 10-fold higher concentration of natural organic matter is present.

The choice of the reactor configuration may affect the possible extension of the processes on a real scale. With supported semiconductors, as is the case with Ti / TiO2-NT, problems can arise for the correct electrode setting, with respect to both counter electrode and light source, which may determine non-optimal current and potential distributions, and poor exploitation of radiation in PEC reactors [50, 51]**. Different performance of NT TiO2 were detected, depending on whether the electrode was placed in a three-electrode becker cell (BC) or in a two-electrode thin gap electrochemical cell [52]*. The greatest differences in performance were found when NT were decorated with TiO2 nanoparticles: the limited accessibility of the electrolyte to the bottom of NT resulted in the exclusion of the contribution of bulk sites to the exploitation of higher wavelength radiation. The specific effects of the structural conformation of NT in terms of electrolyte penetration, diffusion of the reacting species, and absorption of light radiation of different wavelengths in the solar spectrum, have been specifically modeled [53]**. Results indicated that depending on the specific organic compound which has to be treated, different morphologies could be effective. If purification of water is the aim of the process, tubes with 4 mm length or less should be used for low reactive compounds, whereas 2 μm is effective for removal of very reactive compounds, such as phenol. Longer tubes should be considered for wastewater treatment, with high pollutant concentrations.

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 article.

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have been highlighted as:
* of special interest
* * of outstanding interest

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