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Review

More than One Century of History for Photocatalysis, from Past, Present and Future Perspectives

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Abstract: In this review, we analyzed the history and the past and present trends in photocatalysis research, trying to outline possible scenarios for the future in the medium term. The in-depth analysis of the literature reported here—from a mere bibliometric point of view—allowed us to divide the history of photocatalysis into four different periods characterized by different maturity of the topic and different bibliometric features. The turn of the 20th century saw an explosion in scientific production, which is still continuing now and has reached more than 15,000 papers published each year. Research interest is still growing significantly, and the analysis of different keywords suggests that such growth is substantial and not merely due to "publish or perish" behavior. The analysis of the most-investigated topics in the field of photocatalysis highlighted that, during its history, the focus of the research moved from inorganic oxides to carbon and hybrid materials. Concomitantly, the investigation of the "geography" of photocatalysis allowed us to underline its evolution over the years, with the repositioning of its center of mass from the Atlantic Ocean (USA and Europe) to Asia (China and India). Photocatalysis is active as never before but still awaiting major breakthroughs, which would allow a much broader technological and commercial output. Without such breakthroughs in this decade, the growth in scientific interest could level out or even decrease.

Keywords: photocatalysis; environmental application; bibliometric analysis; future perspectives; photochemical processes; photochemistry

Citation: Sordello, F.; Calza, P.; Minero, C.; Malato, S.; Minella, M. More than One Century of History for Photocatalysis, from Past, Present and Future Perspectives. *Catalysts* **2022**, *12*, 1572. https://doi.org/10.3390/catal12121572

Academic Editor: Hideyuki Katsumata

Received: 31 October 2022
Accepted: 30 November 2022
Published: 3 December 2022

1. Introduction

The solar energy reaching the Earth per year is 3,400,000 EJ, and the corresponding total solar flux is equal to 1.08×10^8 GW. At the distance of the Earth from the Sun, the solar constant is 1367 W m^{-2}, and as a consequence of the absorption and scattering of the radiation from the atmosphere, the year/day-averaged energy density at the Earth's surface falls down to 170 W m^{-2} [1]. The impressive amount of energy reaching our planet as electromagnetic energy from the Sun is the real fuel of the Earth, being at the basis of all of the most important cycles (e.g., hydrologic cycle) and processes allowing the existence of highly evolved forms of life on the Earth's surface. The overall primary energy consumption of the human population is estimated roughly as 6000 GW, between 7000 and 8000 times lower than the energy power reaching the Earth. The conversion of the light reaching the surface into chemicals through the photosynthetic process is at the basis of the development of superior organisms and has contributed to the overall definition of the atmospheric composition.

Due to its great potentialities, the conversion of the sunlight into forms of energy easier to be used and stored (i.e., electricity and/or chemical fuels) has been a *fixed idea* of the scientific community since the beginning. The first systematic and scientific investigation of the chemical processes activated by sunlight was dated 1777 with the studies by the Swedish chemist C. W. Scheel who described the violet-light-activated reduction of silver chloride to metal silver. The first principle of photochemistry was defined by the pioneering

works by T. von Grotthuss (1817) and J. W. Draper (1841), who established that *only the light absorbed is effective in producing photochemical change* (the so-called Grotthuss–Draper principle). The main limits for a systematic investigation of the photochemical process in the 19th century were the unavailability of both adequate light sources and analytical techniques; as a matter of fact, the only light source at the disposal of the first scientists that systematically faced the potentialities of photochemistry was the light of the Sun (e.g., G. Ciamician in Bologna [2] and G. Lemoin in Paris [3]).

The idea to carry out a photochemical process in the presence of a compound/material able to catalyze the process itself was proposed at the beginning of the 20th century by Plotnikow in 1910 [4] and Landau in 1912–1913 [5,6]. At the same time, in the 1920s, the first approaches to mimic natural photosynthesis, obtaining both organic compounds (formaldehyde and carbohydrates [7]) by the photochemical reaction between carbon dioxide and water and organic nitrogen compounds by the photoactivated reaction between inorganic nitrogen (nitrate [8] or ammonia [9]) and carbon dioxides, were proposed.

Only from the 1940s were the photocatalytic properties of oxides discovered and investigated, often with the practical aim to increase the life of paints, papers and textiles containing titanium dioxide or other white semiconductors as pigments. In this context, the oxidative ability of certain irradiated semiconductors (e.g., ZnO [10–12], Sb_2O_3 [13,14] and TiO_2 [15,16]) has been investigated, and the potential formation of reactive species such as H_2O_2 has been observed [17–19]. An interesting and didactic review regarding the photocatalytic activity of oxides was published by M. C. Markham in 1955 [20].

Especially in the first part of the 20th century, the term "photocatalytic reaction" was often used with a more general meaning of "photochemical reaction"; as an example, in the seminal works by Baly et al. cited above [7–9], the chemical reactions investigated were photochemical processes but not photocatalytic ones, because no catalyst was added in the reaction medium to accelerate the kinetics of the process. In fact, in agreement with the recognized IUPAC definition [21], in a photocatalytic reaction there is always "the presence of a substance—the photocatalyst—that absorbs light and is involved in the chemical transformation of the reaction partners"; furthermore, the photocatalyst must regenerate its chemical composition and properties after each catalytic cycle.

Only from the late 1970s did the photocatalytic processes start to be investigated as effective tools to solve environmental problems. In particular, this was conducted in the field of energetics with the seminal works by Fujishima and Honda on the photo-assisted electro-splitting of water on titanium dioxide electrodes [22] and by Inoue et al. on the photocatalyzed reduction of carbon dioxide on irradiated semiconductors [23] and as an effective tool for environmental remediation especially for (i) the removal of recalcitrant pollutants from water [24–26], (ii) the degradation of air pollutants [27] and (iii) the inactivation of pathogens [28].

The history of photocatalysis can be divided in different ways; as an example, the quite effective division proposed by Serpone and Emeline [29] as a function of the type of materials used to carry out the photocatalytic processes is often cited. In particular, three different generations of photocatalysts have been proposed. The first is composed by pristine inorganic semiconductors (in the beginning mainly ZnO, WO_3 and TiO_2 and then mainly TiO_2 only), of which the photocatalytic properties have been investigated in depth, often with pioneering experimental approaches, with the main aim to give insights into the mechanism of production and transfer of the charge carriers generated inside the material and into the nature of the reactive species operative in the investigated photocatalyzed processes. The second generation of photocatalysts is mainly composed by doped semiconductors synthesized to push the onset of absorption toward longer wavelengths introducing intra-bandgap states, the nature and energetic positioning of which have been deeply investigated, even though the first report of their discovery remained unnoticed for a long time, [30] while a successive report received more recognition (and 16 times more citations!), being the most cited photocatalysis paper of its decade (vide infra) [31]. The doping strategies proposed were based on the introduction of non-metal

or metal centers inside the crystallographic structure of the pristine material with the aim to generate color centers (localized states located between the valence and conduction bands [32–34] and/or oxygen vacancies with the formation of centers where the metal cations have different oxidation states, e.g., Ti^{+3} centers in a TiO_2 structure [35,36]). The third and last generation proposed is based on the production of hybrid heterostructures formed by two or more inorganic semiconductors [37–39]. In this case, the dynamics of the charge carriers became extremely complex, especially if the number of the materials composing the hybrids is higher than two. In some cases, these photocatalysts have shown both high efficiency and a better ability to harvest solar irradiation with respect to the pristine and doped semiconductors.

After the synthesis of the new synthetic carbon allotropes (fullerenes [40], carbon nanotubes [41] and graphene [42]) and of their almost infinite modifications, a new class of photocatalysts has been proposed and commonly denoted as metal-free photocatalysts. These materials, either used as is or coupled with inorganic heterostructures with different complexity, have been proposed in all the application fields of the photocatalysis. Recently, some of the authors of this article have questioned if these new materials can be or cannot be considered as the fourth generation of photocatalysts [43]. Overlooking this purely semantic point, it is essential to note that the efforts of the community operating in this field are actually mostly directed at the development and testing of these materials that represent, without any doubts, the most fascinating (or the most in-fashion) topic in the field of photocatalysis.

The aim of the present article is not to give an exhaustive evaluation of the entire literature regarding photocatalysis, since for this purpose some excellent reviews have already been published both recently [44,45] and in the past [46,47]. A fully complete analysis of the actual literature, as underlined on the basis of a detailed bibliometric analysis reported in the following paragraphs, if possible, up to the initial 2000s, is impossible nowadays, due to the impressive number of papers published every year. Using as a keyword "photocatal*", an exhaustive database such as Scopus returns more than 15,000 entries per year, nowadays (see Figure 1). So, to give insights into "photocatalysis" as a scientific topic and to obtain general considerations regarding its past, present and future, we carried out an investigation starting from an in-depth analysis of the most important works published in the first period of the development of this topic and moved gradually to a less detailed evaluation of the literature based on an overall vision of the entire production by using general bibliometric descriptors. With this approach, we propose to divide the entire history of photocatalysis into four blocks, not on the basis of the nature of the photocatalysts investigated, as proposed by Serpone and Emeline and described here above [29], but on the basis of the degree of development of the scientific thinking and of the research regarding the photocatalyzed phenomena.

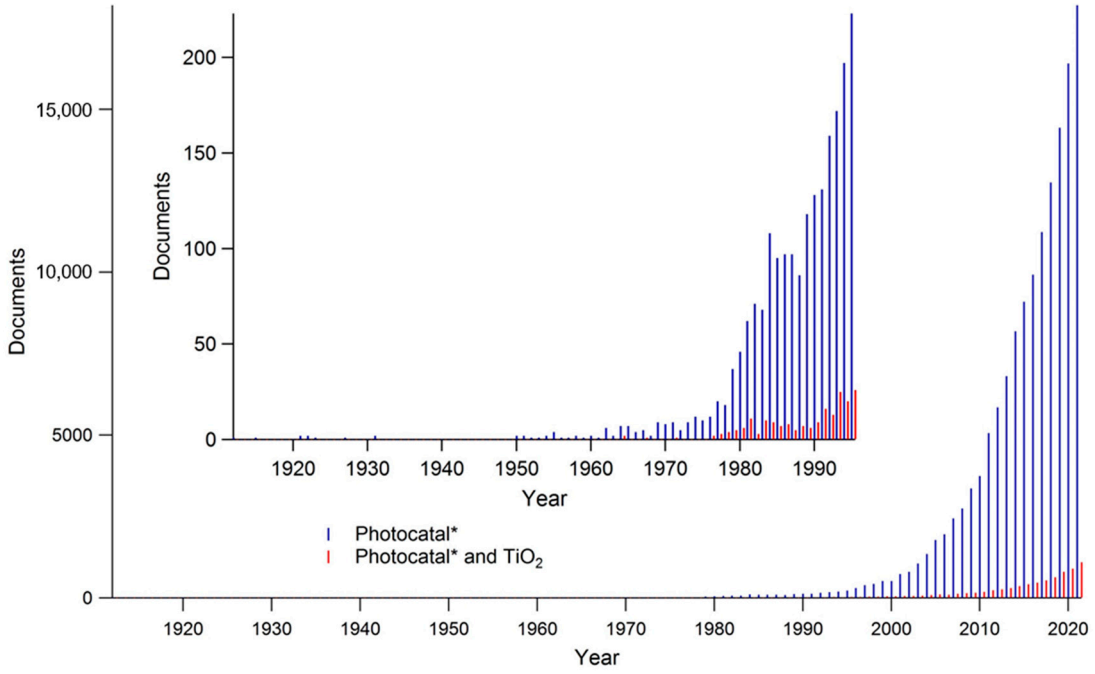

Figure 1. Number of published documents (database: Scopus, 20 September 2022) per year indexed as "*photocatal**" and "*photocatal * and* TiO_2". Insert: zoom from 1912 to 1995.

2. Bibliometric Analysis of Photocatalysis as a Scientific Topic: Temporal and Geographic Analysis

To give insight into the field of photocatalysis as a scientific macro-topic, a first tool is the analysis of the number of works published on this theme since the beginning.

The Scopus database (September 2022) has been used as the source of the desired information. Figure 1 shows the number of documents published since 1912 and indexed with "photocatal*"; moreover, what is also reported is (i) the number of reports dedicated to the photocatalytic properties of TiO_2 ("photocatal* AND TiO_2") and (ii) a zoom regarding the data from 1912 to 1995. From 1912 to 1973, the number of articles published per year on photocatalysis was less than 10, from 1974 to 1988 less than 100, from 1989 to 2002 less than 1000 and, finally, from 2003 and 2016 less than 10,000. Since 1974, it an increase in the number of published articles of an order of magnitude every 13/14 years has been observed. From 2016, the number of articles is over 10,000, with a monster number of 18,196 documents in 2021. At the same time, the relative weight of the works on the photocatalytic properties of TiO_2 has changed, being before 2000 almost 10–12% of the overall documents and in the range 4–8% from 2000 to nowadays. This is a clear index of the shift of the attention towards different materials with respect to the semiconductors of the "first generation", even if titanium dioxide continues to be investigated and used as a functional material also in hybrid structures [48,49].

These numbers must be also considered in the light of the overall explosion (with the beginning of the 21st century) of the scientific productivity in states (i.e., China and India) that were marginal before 2000.

From the overlap of the main topics investigated and of the number of published documents, we propose here to divide the history of photocatalysis into four different periods: (i) the *Pioneering years* (until 1980) with less than 50 publications per year mainly dedicated to the fundamentals of photocatalytic phenomena, (ii) the *Maturity* (1981–1995) with less than 300 articles per year related to the better understanding of the operational mechanisms and to the investigation of the potential applications (especially in the field of the removal of pollutants in water), (iii) the *Explosion* (1996–2010) with less than 5000 articles/year dedicated to the most different topics with a peculiar focus on the increment of the quantum yield of the process and the extension of the exploitable spectral windows,

(iv) the *Inflation* (2011–) with an almost complete attention to innovative materials and in particular to hybrid structures with the aim to exploit the properties of the junctions among different inorganic/organic materials, especially for energy applications (H_2 production, CO_2 reduction and artificial photosynthesis). While the knowledge of the most relevant scientific literature on the topic required reading three or four papers per month in the 1980s and early 1990s, at the turn of the century it became a much more difficult task, which eventually turned into an impossible job in the latest 20 years.

It is interesting to observe the change in the relative distribution of the affiliations (in terms of country of origin) of the authors for each period. For this reason, the works indexed as "photocatal*" have been divided into the different temporal periods, and the affiliation countries have been compared. Figure 2 shows the relative weight of each country from the *Pioneering years* to nowadays. The first four countries accounted always for more than 50% of all the publications, but the relative positioning changed with the years. The USA moved from the first contributing country until 1980 with more than 36% to the actual third position, with an average weight equal to 8.8%. Japan had a peak of weight in the *Maturity* period (21.5%) that is nowadays reduced to 3.8%. The relative weight of the European countries, which accounted for roughly 20% of the overall publications until 1995, decreased to roughly 12% in the *Explosion* period and to ≈8% in the *Inflation* period. Conversely, the contribution of China and India that accounted for less than 5% until 1995 is now higher than 45%.

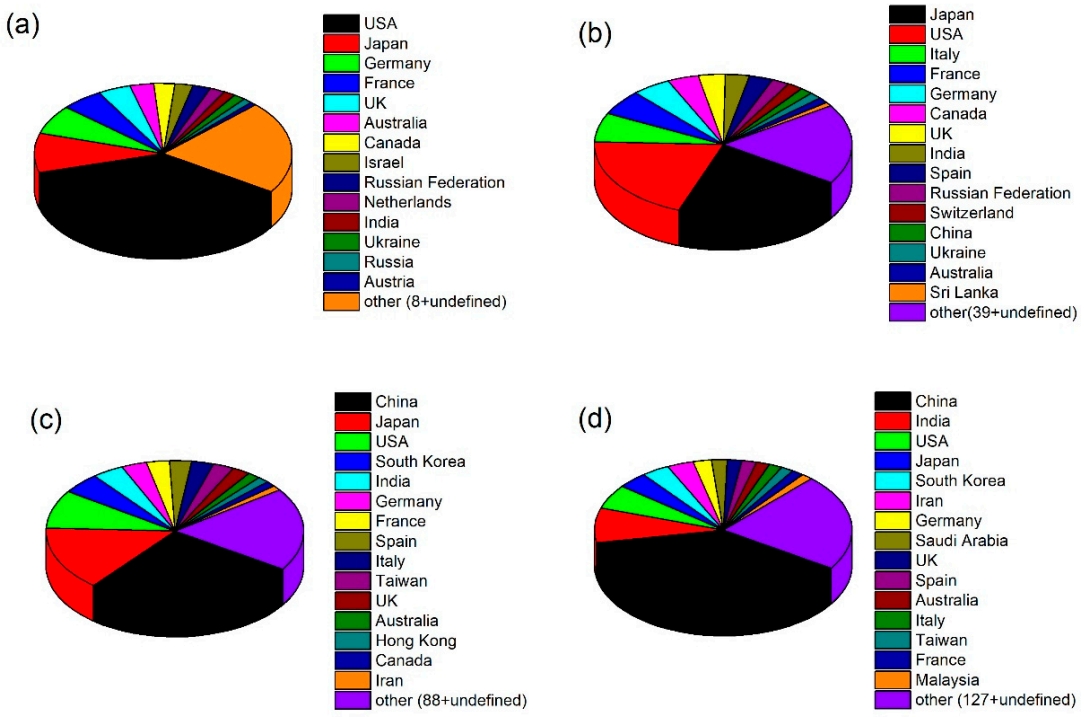

Figure 2. Relative weight of the affiliation country for the documents indexed as "photocatal*" divided into the four periods proposed: (**a**) Pioneering years (until 1980), (**b**) Maturity (1981–1995), (**c**) Explosion (1996–2010) and (**d**) Inflation (2011–2021) (database: Scopus, 20 September 2022).

The papers published in the field of photocatalysis ("photocatalysis" in the title, abstract or keywords) are still increasing every year, and this increase is still exponential, as witnessed by the linear trend observed in the logarithmic plot of Figure 3. The growth was even faster between 1990 and 2000. Searching the database with slightly different keywords (e.g., "photocatalysis and semiconductor" or "semiconductor photocatalysis") leads to very similar trends, although with a different number of published documents.

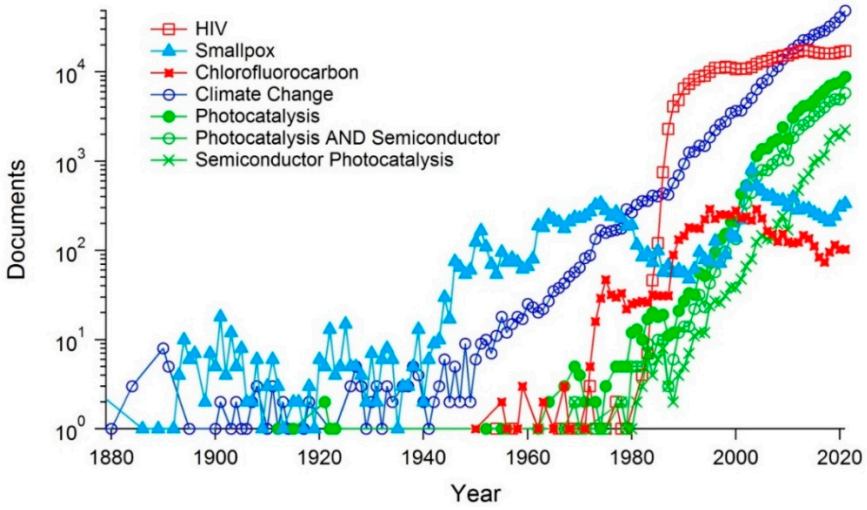

Figure 3. Number of published documents per year as functions of the publication year for several keywords.

Nonetheless, the scientific literature is inflating in many different fields; therefore, we asked ourselves if the growth in the field of photocatalysis is really significant and not just reflecting different habits in the researchers' behavior towards publishing. The best figure to make this assessment is the total number of published documents in the whole scientific literature. Unfortunately, this number cannot be obtained with sufficient accuracy; therefore, we compared photocatalysis with other keywords. Keywords such as "smallpox" and "chlorofluorocarbon" represent fields of research which should have reached their maximum interest in the past, as the last documented smallpox case dates 1979, and the Montreal protocol forbids the further production of chlorofluorocarbons. A significant increase in the published documents in the latest two decades on these two topics would only reflect different habits in the behavior of the researchers, who are becoming more willing to publish and not because of recent breakthroughs in the field. In fact, for "smallpox" and "chlorofluorocarbon" we can observe a decrease in the published documents in recent years.

A keyword such as "HIV" represents a topic which is still researched, as the quest for cures and vaccines is still very active; nevertheless, the insurgence of the disease dates back to the early 1980s. In this case, after a fast growth in the late 1980s, we can observe two phases of linear growth in the early 1990s and 2000s interrupted by two periods of almost constant scientific production in the late 1990s and 2010s.

With "climate change", we wanted to consider a very popular research field. The interest in the topic is not very recent, as since 1954 at least 10 documents have been published every year. Since then, the publications increased exponentially with an almost constant rate. Since 2000, the trends of "climate change" and "photocatalysis" run almost parallel with almost exponential growth. We can therefore conclude that the scientific interest in the field of photocatalysis has been increasing at a steady and impressive rate for 35 years, and researchers are continuing to join the field and give their contributions, positioning photocatalysis among the most important topics in the field of chemistry and material science, especially for its remarkable potentialities for the resolution of worldwide environmental problems.

This comparative analysis between photocatalysis and other selected topics can also be carried out from a geographical point of view; for this reason, we elaborated the data reported in Figure 3, splitting the overall number of published documents as a function of the affiliation country of the authors. Concerning the geography of photocatalysis, which has already been discussed above considering its time evolution, we can highlight that Asian institutions are the most productive (Figure 4e). Among the top-five countries, four are Asian, namely China, India, Japan and South Korea; furthermore, Iran is the

eighth most productive country. This trend is similar to that found for an emerging chemistry research project, MXene, for which 8 of the top-12 publishing countries are Asian (Figure 4g). Comparing photocatalysis with the other keywords considered before, the role of North American and European countries becomes predominant. On the one hand, this can be attributed to the recent involvement of Asian countries compared with North America and Europe; on the other hand, the contribution of Western countries seems greater in medicine-related topics compared with chemistry and material science. Among European countries, the United Kingdom (UK) is usually the leading country in almost all the examples here considered, with the notable exception of photocatalysis. In chemistry-related fields, Germany immediately follows the UK, while Italy and France look more competitive in medical research. Photocatalysis appears to be the exception to this rule, with limited contribution from the UK (and USA) and with Germany and Spain as the main European contributors.

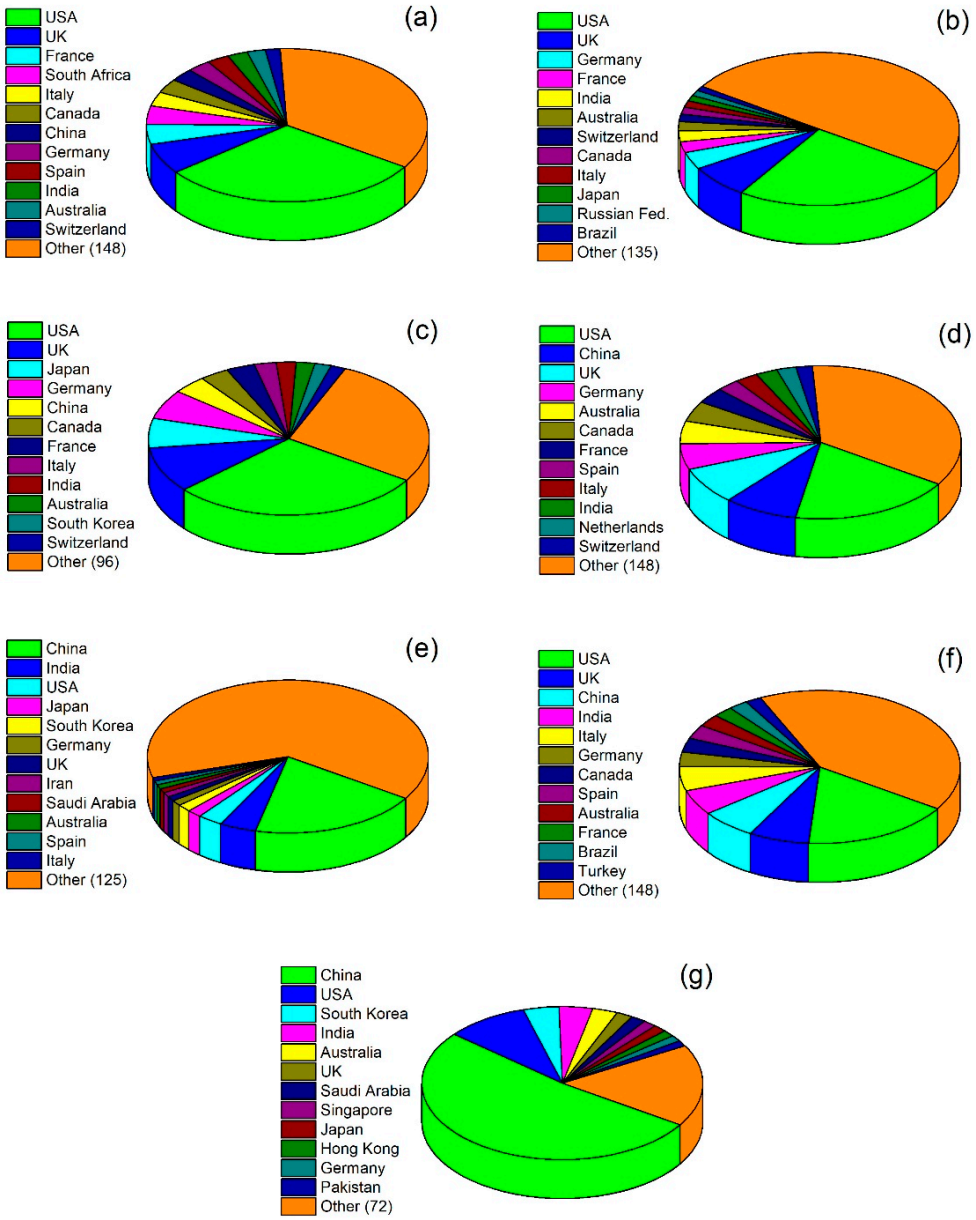

Figure 4. Pie charts representing the share of documents published by country (i.e., researchers affiliated to institutions of each country) by keywords: (**a**) HIV; (**b**) smallpox, (**c**) chlorofluorocarbon; (**d**) climate change; (**e**) photocatalysis; (**f**) COVID-19; (**g**) MXene.

3. Evolution of the Main Topics in the Field of Photocatalysis

Coming back to the previously defined four periods of photocatalysis, the number of the total publications in each group will be dramatically different, due to the exponential growth of the published documents. Keeping in mind that a comprehensive synthesis of the whole literature has become an impossible task in the last 20 years, we tried to give a critical assessment of the past activities and possibly outline future trends.

We therefore analyzed the 20 most-cited documents, with review articles excluded. Nonetheless, relevant review articles which were cited more than the 20th most-cited paper were considered separately. The publication and the success of review articles are indeed very informative about each period of time considered. This piece of information, together with other data presented in Table 1 and the most relevant keywords, allowed us to associate to each period of time several prominent research goals:

Table 1. Overview of the main bibliometric indexes regarding "photocatalysis" divided into the four temporal blocks.

Years	1800–1980	1981–1995	1996–2010	2011–Present
Name	**Pioneering Years**	**Maturity**	**Explosion**	**Inflation**
Citation trend last 5 years	Increasing	Decreasing	Decreasing	Increasing
Relevant reviews	4	9	24	61
Citations (% before 2018)	9149 (75%)	13,889 (89%)	61,836 (73%)	36,235 (40%)
Citations/Papers	457	694	3092	1812
Citations [a] (% before 2018)	11,112 (74%)	51,517 (84%)	143,139 (66%)	156,429 (32%)
Citations/Papers [a]	463	1776	3328	1931
Citations 1st	1993	1947	11,488	4816
Citations 20th	145	501	1658	1187
Median citations	350	589	2053	1461
Median of the year of publication	1978	1991	2004.5	2012.5

a: With relevant reviews.

1—Until 1980, the *Pioneering Years*. In this first period of time, 0.07% of the documents were published. The main research interests concerned the mechanism, the demonstration of functionality and the addition of co-catalysts such as metals and RuO_2. The global picture was dominated by TiO_2, but $SrTiO_3$, CdS and ZnO were also investigated, and they appear also in the top-cited papers. Researchers' attention was devoted also to the production of H_2, CH_4 (photo-Kolbe) and to CO_2 and N_2 reduction. Review papers were general and focused on principles and the mechanism of the process. [50–72]

2—1980–1995, *Maturity*. In total, 0.49% of the documents were published in this period. The research was directed towards the kinetic analysis, metal doping, pollutant removal and structural studies regarding quantum effects on semiconductors. TiO_2 gained a much more prominent role than in the previous period of time. General reviews were joined by more specific reviews considering sub-fields such as environmental applications, water purification and energy applications. [73–99]

3—1996–2010, *Explosion*. In total, 16.6% of the documents appeared in that period of time. The research concerned non-metal doping (C, N, F), heterostructures, the fabrication of Z-schemes with multiple materials and CO_2 utilization. TiO_2 predominance started to be challenged by C_3N_4 and ternary semiconductors such as $BiVO_4$. Reviews started to represent the majority of top-cited papers,

and they were focused on specific aspects (e.g., surface properties, disinfection, degradation of specific classes of compounds) and on recent advances. [100–138]

4—2010–present, *Inflation*. In total, 82.8% of the documents were published in this most-recent period of time. The research expanded towards plasmon resonance, and carbon-based materials (graphene, C_3N_4, C quantum dots) became predominant, both alone and in composites. TiO_2 is still the most studied among oxide materials, usually in combination with other materials. Many elements are now considered Mo, Cd, In, Ga, Ag, Ce, W, C, N, F, S, O, Bi, V, Zn, Cu, Fe, . . . , even if crustal abundance considerations would suggest limiting the research on abundant and inexpensive elements (vide infra). Reviews represent more than 75% of top-cited papers, and they are mainly focused on recent advances, on sub-topics (Z-scheme, WPS, CO_2. . .) and on particular material classes (e.g., specific metal oxides). [139–219]

From the analysis of the most-cited documents (Table 1) within each period, several considerations emerge:

- In periods one and two, more than 60% of the most-cited documents were published in the last 5 years considered. This is also due to the exponential growth of the production with time, because there are more recent papers to cite.
- During the *Inflation* period, the median year of publication is 2012.5, very close to the beginning of the period considered (2011). Even though the time available for the most recent articles is limited, the consideration made before is still valid, and the papers published in 2011–2013 are much less than in 2018–2020, as an example. Another important factor could be the difficulty to find, read and cite a specific paper in the gigantic and increasing scientific production. Recent papers could be less cited than expected because they are not known by the whole community
- Citations before 2018 highlight that, besides the obvious trend for the most recent period, papers form the *Pioneering Years* are still popular and reasonably cited, as 1/4 of their citations arrived in the last 5 years, a trend shared with the *Explosion* (1996–2010). Conversely, only 14% of the citations arrived in the last 5 years of the *Maturity* period. Those documents were already very modern, and it is the authors' opinion that they should receive more recognition in the present literature. Unfortunately, it is sometimes preferred to cite more recent papers to give the idea of cutting-edge research, with few references to the noble and pioneering investigations, completely neglecting instead a whole body of relevant and rigorous research, whose size—in terms of published documents—still allows its almost complete knowledge.

Besides the top-cited papers for each single period of time, there are documents which paved the way to new research lines, but, even though their seminal nature has been recognized by a generous amount of citation, usually more than 300–400, they do not appear in the list of the 20 top-cited articles. We identified at least four representative domains:

- Reduction reactions promoted through photocatalysis [220,221]. This field could regain popularity in the near future because of the emerging concern on PFAS pollution, which has recently been assessed as beyond planetary boundary [222]. PFAS are not emitted in significantly larger amounts compared with other pollutants; nevertheless, their inertness makes them extremely persistent in the environment, and their environmental impact and mitigation costs are therefore relevant [223]. Reduction of the C-F bond through semiconductor photocatalysis could represent an effective strategy for their removal from the environment and especially to prevent their dispersion. Furthermore, a better comprehension of the reductive photoactivated processes could be essential for a better comprehension of processes potentially important for energetics, such as the water photosplitting, the production of hydrogen through reforming of organic by-products or residual biomasses, the CO_2 photo-reduction and the artificial photosynthesis [214,224,225]. Moreover, reductive processes activated by irradiated

semiconductors have been proposed both in the *Maturity* period and nowadays for the recovery of precious or critical metals from diluted solutions [60,88,226–230].

- Surface modification by fluorination [231,232] was found to deeply modify TiO_2 behavior in F^--containing solutions, [233] because of its strong adsorption on {001} facets and defective sites [234]. This led to a new field of investigation concerning the engineering of TiO_2 nanoparticles, as fluorides could act as powerful shape controllers during hydrothermal synthesis [235]. The resulting nanoplatelets now find applications in different fields, e.g., nanometrology [236].
- Different crystalline facets' reactivity demonstrated by Ohno and coworkers [237], which elegantly demonstrated how {101} facets in anatase and {110} facets in rutile are able to more efficiently trap electrons and therefore promote reduction reactions, whereas {001} facets in anatase and {011} in rutile preferentially trap photoholes and therefore promote oxidation reactions, e.g., PbO_2 deposition from aqueous Pb^{2+} in the original work. This concept has been confirmed and exploited at several reprises, and it represents one of the main strategies to improve the efficiency of the photocatalytic process [238,239].
- Mechanistic studies of semiconductor photocatalysis. Even nowadays, several decades after the pioneering investigations in the field, errors and misconceptions around the working mechanism behind semiconductor photocatalysis are still present and widespread in the specialized literature. One of the most common examples is the interpretation in terms of substrate adsorption of the non-linear growth of substrate removal rate as a function of its concentration. Even if the Langmuir–Hinshelwood isotherm is still frequently reported to justify such a behavior, this explanation has no real physical significance, as elegantly observed by Emeline et al. [240] and formally demonstrated through quantitative kinetic modeling at several reprises [241–246].

4. Present Situation and Future Challenges

To analyze the actual hot topics in the field of photocatalysis, the following approach was adopted. By taking into account the five years 2017–2021, we selected the top 15 most-cited articles (excluding the reviews), and we categorized these articles as a function of the keywords that better described each paper. This approach is able to select the topics on which the scientific community paid more attention that could not necessarily be the topics essential to go ahead both in the comprehension of the phenomena (from a mechanistic point of view) and in the technological exploitation of the process. Furthermore, this classification of the actual main topics has been split in an analysis devoted to the photocatalytic process and phenomena (Figure 5a) and in another one dedicated to the investigated materials (Figure 5b).

Regarding the photocatalytic process investigated, currently the main attention is related to the photocatalytic production of hydrogen, while both the photocatalytic reduction of CO_2 and the traditional removal of pollutants are investigated at the same level and roughly in half of the cases with respect to those dedicated to the H_2 generation. The photocatalytic production of ammonia from molecular nitrogen continues to be a niche topic mainly for the intrinsic difficulty to activate the stable triple covalent bond of N_2.

From the point of view of the mechanism and of the general features of the photocatalytic phenomena, the main attention is driven by the construction and properties of heterostructures (in hybrid photocatalysts) where Z- and S-schemes [247] are operative with the aim to optimize the quantum yield of the process, maximizing the charge carrier separation. At the same time, huge attention is placed on the production of visible-active photocatalysts. On the contrary, topics such as plasmonic photocatalysis, photocatalytic disinfection, the green synthesis of complex compounds and molecular oxygen activation have intercepted a lower number of citations.

On the side of the most-investigated photocatalytic materials, a plethora of compounds is now investigated, and only a limited number of materials are significantly more frequently used. g-C_3N_4 is currently the most-studied material, while the role of graphene

and graphene oxide (GO) as functional materials is nowadays dramatically decreased with respect to the impressive attention generated after its discovery and first applications. From the point of view of the most-studied "classic" semiconductors, TiO_2, WO_3, CdS, bismuth-based semiconductors and ZnO are the most investigated. Emerging materials are the MXene materials, quantum dots, the metal organic framework (MOF) and 2D phosphorus (black phosphorous and phosphorene).

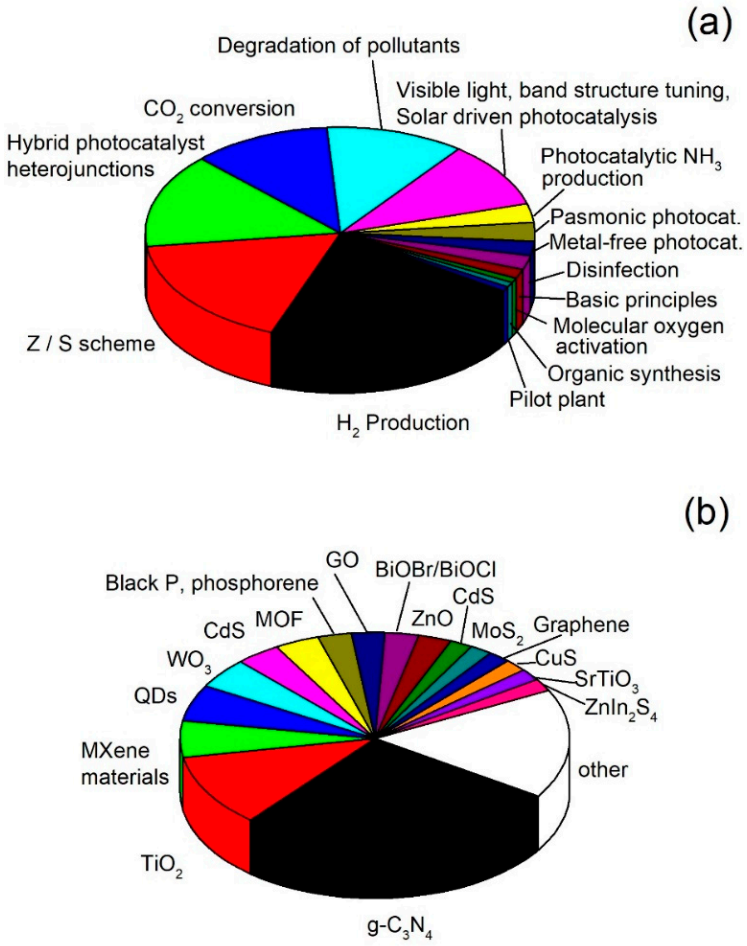

Figure 5. Evaluation of the main topics (**a**) and most-investigated materials (**b**) in the field of photocatalysis in the period 2017–2021.

Next to these more investigated, fascinating and in-fashion topics, there is in our opinion a forgotten topic that is actually far from the overall attention but is actually of pivotal importance. This is the investigation of the photocatalytic technologies in real contexts and at a dimension higher than the lab-scale. Proof of this scarce (almost null) attention comes from the comparison of the works published in the field of photocatalysis dedicated to tests at pilot-plant scale. Of the 158,950 documents found on the Scopus database (September 2022) by using as a keyword "photocatal*", only 300 works (reviews included) are indexed as "photocatal* AND pilot-plant". For an absolute mature scientific theme with important potential applications such as photocatalysis, this scarce attention to the real applicative aspects can for sure be considered a bottleneck in its development. Interestingly, only three countries (Spain, Italy and Portugal) contributed more than 2/3 to the production of these 300 documents. This geographic "anomaly" can be closely related to the scarce diffusion in the world of big infrastructures dedicated to solar photochemistry. In this light, the Plataforma Solar of Almeria (Spain), inserted in the framework of the European infrastructure of the research, is a praiseworthy exception.

5. Conclusions and Perspectives

If we observe the topic of photocatalysis from the beginning to nowadays, this sector will appear with a high level of scientific development thanks especially to the contributions of the *Maturity* period (1981–1995) from some consolidated research groups located mainly in the USA, Japan and Europe (Italy, France, Germany, the UK and Spain) that mainly clarified from a theoretical point of view the operative mechanism of the photocatalytic processes. On the contrary, the exploitation of these processes in technological applications is still far off, both for energetic applications (e.g., water photosplitting, reforming of organic compounds and photocatalytic CO_2 reduction) and for the removal of recalcitrant pollutants. The only exception is the application of the photocatalytic process for the air depuration/disinfection. Photocatalytic cements are currently on the market [248,249] together with photocatalytic devices able to promote the degradation of gaseous pollutants or deactivation of pathogens [250,251], often with the concomitant application of the photocatalytic technology with ozone and/or UV photolysis (the market of these devices was boosted during the COVID-19 pandemic for obvious reasons). Moreover, on the market there are actually some examples of (i) superwettability and antifogging devices (e.g., mirrors for the automotive sector) based on the covering of a surface with photocatalytic coatings becoming superhydrophilic under irradiation; and (ii) antimicrobial surfaces able to abate the proliferation of pathogens activating the photocatalytic production or reactive species. In particular, investigations of the photocatalytic technologies in large pilot plants are scarce, and this hinders a clear evaluation of all the real potentialities of the photocatalytic technologies.

Interesting and demonstrative is the fact that despite the impressive number of published articles per year and the gigantism of the topic, the Nobel Prize in Chemistry has never been awarded to scientists that have operated in this field. This can be also due to (i) the fact that the scientific knowledge on this topic has been created more with a diffuse activity of different groups of research than by the work of a single scientist, (ii) the presence of only niche applications for photocatalysis has not had impressive consequences on society (as an example, the broad application in everyday life of lithium batteries was for sure at the basis of the appointment of the Nobel prize in Chemistry in 2019 [252,253]).

From our analysis, three main possible scenarios for photocatalysis can be envisaged in the medium term:

1. Reduced involvement and reduced scientific production as a consequence of the development of alternative technologies. Examples could be (i) the production of hybrid technologies able to very efficiently convert the sunlight into electricity through photovoltaics and to store this energy in super electrochemical capacitors (and/or other energy storage systems), making useless the photocatalytic production of high energetic vectors such as H_2; (ii) the development of very efficient and scarce energy-demand membrane technologies able to easily remove pollutants from water, creating a market for photocatalytic technologies for the removal of biorecalcitrant pollutants; (iii) for the specific application of effluents decontamination and disinfection, the exponential growing of renewables energies for the production of electricity would impulse other technologies based on ozonation, UVC and other electricity-based processes that have substantially reduced their environmental impact.
2. Almost constant involvement of the researchers, as the research on photocatalysis continues without any major breakthrough and the sector maintains good relevance in the fields of chemistry and material science, reaching a physiological limit in the number of publications mainly related to the limits and rules of the editorial scientific markets.
3. Continued increase in the involvement of new research groups attracted by one or more breakthroughs within the traditional research lines in photocatalysis (e.g., synthesis of catalysts with a quantum yield near one operative in the visible spectrum) or outside it (e.g., production of UV irradiation systems at dramatically low cost and with very low energy requests or increment of the cost of competitor technologies

of photocatalysis). In this way the photocatalytic technologies could reach a high technology readiness level (TRL), paying back the impressive scientific efforts carried out—since the beginning—on this topic from generations of scientists.

A conclusive remark must be made on the importance to develop photocatalytic technologies that take into account the real availability of the elements in the earth's crust [254]. The suggestion is always to focus on materials and technologies not based on the use of critical raw materials: for photocatalytic technologies to be a successful "story", they cannot be in competition with other technologies for the same elements (especially if critical [255]) and must not be limited by the crustal availability of the elements essential for their implementation.

Author Contributions: Conceptualization, F.S. and M.M.; writing—original draft preparation, F.S. and M.M.; writing—review and editing, P.C., C.M. and S.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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