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Science mapping of TiO₂ modification strategies for wastewater treatment: Current and future trends

M. R. Khan¹, H. Abdullah², W. Safiei³, Z. B. Handani², R. R. Nasaruddin⁴, M. N. Arifin^{2*}

¹ Petroleum and Chemical Engineering Programme, Faculty of Engineering, Universiti Teknologi Brunei, Jalan Tungku Link Gadong, BE1410 Brunei Darussalam.

² Faculty of Chemical and Process Engineering Technology, Universiti Malaysia Pahang Al-Sultan Abdullah, 26300 Gambang, Pahang, Malaysia.

³ Faculty of Manufacturing and Mechatronic Engineering Technology, Universiti Malaysia Pahang Al-Sultan Abdullah, 26600 Pekan, Pahang, Malaysia.

⁴ Department of Biotechnology Engineering, Kulliyyah of Engineering, International Islamic University, 50728 Kuala Lumpur.

*E-mail: noormd@umpsa.edu.my

Abstract. TiO₂ is the most widely used photocatalyst owing to its advantages, such as exceptional surface area, stability, and high surface activity. However, TiO₂ suffer from a wide band gap and high recombination rate of charge carriers. This research assesses the knowledge structure of the various strategies adopted to modify titanium dioxide (TiO₂) for wastewater remediation. Capitalizing VOSviewer software, a bibliometric analysis was performed on 898 articles extracted from the Web of Science (WoS) database to determine the intellectual structure of collected documents. Three major clusters were generated through bibliographic coupling and four from co-occurrence analysis, from which the emerging and future trends of TiO₂ modification approaches were determined, respectively. Bibliographic coupling highlighted three key clusters on the emerging trends of the TiO₂-modification technique. The analysis revealed that the current trends focus on the utilization of copper-based dopants in TiO₂, demonstrating improved charge isolation and visible light activation. The second cluster underscores the noble metal doping, with gold and silver compounds leveraging localized surface plasmon resonance (SPR) properties. The third cluster explores graphene-based co-doping strategies. Co-occurrence analysis of 56 high-frequency keywords revealed four thematic clusters centres on nanocomposites for pollutant treatment, integration of adsorption, photocatalysis and advanced thin-film deposition techniques. The significance of this study lies in its potential to guide researchers in exploring identified nanocomposite materials and techniques to enhance the efficiency and properties of TiO₂ for the photodegradation of organic molecules in wastewater.

1. Introduction

The increasing amount and complexity of wastewater causes serious health and environmental problems, posing the requirement of developing suitable and sustainable water treatment technologies. With distinguished properties, TiO₂ has exhibited excellent based material properties, making it the primary material as a photocatalyst. TiO₂ is the readily useable, most economical, and well-profiled UV light active photocatalyst [1]. The photoutilization of TiO₂ is, however, bogged down by its wide band gap (approximately 3.2 eV) and high charge recombination rate, resulting in the utilization of



approximately less than 5% of the whole solar energy [2,3]. Researchers have proposed and tested several strategies to overcome these limitations by tuning specific properties of pure TiO₂. The main purpose of altering the electronic features of TiO₂ is to elevate the light absorption and save the electron from recombination with the holes or lost as heat. Overwhelming works have been reported on enhancing TiO₂ properties via numerous strategies. Despite the extensive research, there is still no clear consensus on the most effective and common modification approaches for wastewater treatment. The diversity of modification techniques, ranging from doping to composite formation, makes it challenging to identify the optimal strategies that offer high efficiency and long-term stability.

One of the most widely adopted strategies is doping TiO₂ with metals and non-metals components, forming nanocomposite photocatalysts [4]. The doping materials usually applied in the synthesis process range from metals to metals [5]. Via metallic ions-doped, the light absorption quantum of TiO₂ is broadened, which elevates the electrochemical potential of generated radicals and improves the light absorption efficiency [6]. The newly formed heterojunction structure prevents the recombination of charge carriers from the conduction band to the semiconductor's valence band [7]. Among the literature that has reported on the doping of metallic ions include copper (Cu) [8–10] cobalt (Co) [11,12] and iron (Fe) [13,14]. Besides metal, non-metal doping has also been exercised where a non-metal element is introduced into the crystal lattice of the as-synthesized photocatalyst. In this technique, the non-metal element reacts with oxygen atoms, modulating the electron cloud density by modifying their bonding or electronic environment [15,16]. This is typically due to the electronegativity and hybridization of the dopant with oxygen atoms. This adjustment separates the atomic energy levels of oxygen, inducing the existence of localized states and creating an intermediate bandgap in the primary catalyst [17]. As a result, the range of light wavelength for absorption is widened for the utilization of photocatalysis [18].

Apart from transition metals, noble metals have also attracted researchers due to their ability to improve the physicochemical properties of TiO₂ by incorporating a plasmonic effect and increased conductivity [19]. It was reported that the surface modification technique by using noble metals, for instance, silver (Ag) and gold (Au), empowers the ability of TiO₂ to harvest solar light through SPR [20], hence enhancing the photocatalytic performance of TiO₂ to degrade organic pollutants. Besides doping, zero-dimensional point defects (ZDPD) are another method that has been applied to modify TiO₂ through vacancy and impurity [21]. Oxygen vacancy is created by eliminating the lattice of oxygen atoms, resulting in the formation of coordinately unsaturated (CUS) metal atoms and the build-up of surplus electrons [22]. The position of CUS metal can be either in an electron-rich state or at a lower level.

A review of the various strategies for modifying TiO₂ was presented for the applications in water treatment photocatalysis [23]. The fundamental concepts of altering the properties of TiO₂ covered are surface modification, including deposition with metal nanoparticles, elemental doping, acids modifications, heterojunction, metal ion implantation and dye sensitization. The scope of the review includes water splitting, CO₂ conversion and pollutant remediation [23]. Another review work reveals the modification of facet-engineered TiO₂ [24]. The highlights of this work uniquely touch on the significance of specific facets of the fabricated crystals on the TiO₂ photocatalytic performance. Different TiO₂ facets constituted distinct atomic and electronic structures, leading to distinguished optical properties and adsorption capacities for CO₂ and water. An impressive review of the TiO₂ modification works was particularly conducted, unveiling the mechanisms and the disadvantages of every modification strategy of TiO₂ [25]. This work focuses on the current advances and future potential of particularly dye-sensitization photocatalytic systems (DSP). It was noted that the recent advances in DSP include efficiency improvement by manipulating hydrophobic and/or hydrophilic properties and controlling the dye organization of the surface of the photocatalyst.

Since 1993, the keywords/phrases “metal doping”, “surface modification”, “non-metal doping” and “noble metal” with additional keywords; “TiO₂” and “photocat*” and (degradation OR wastewater OR treatment) have been sought in the web of science (WoS) database results in 2838, 1221, 191 and 183 documents respectively, without limiting to any specific type of wastewater. Therefore, the quantitative assessment of the impact, trends, and research development in photocatalytic treatment of wastewater over TiO₂-modified photocatalysts is urgently needed. The main purpose of this bibliometric analysis review is to thoroughly examine the current advancements in TiO₂ modification strategies for wastewater treatment. By evaluating the breadth of the literature on this topic, we aim to determine the prevailing trends and study the impact of various modification techniques. The results from the bibliographic coupling analysis enable us to draw the gaps in the current research potential. The co-occurrence analysis unveils future research directions and serves as a guide to photocatalytic-related researchers.

Despite many reviews on the TiO₂ modification techniques, few studies concentrate on assessing the knowledge structure through science mapping. No study employing science mapping has been reported on the TiO₂ modification strategy for the photocatalytic treatment of wastewater, except a few works which discuss the performance analysis of the related works such as the information on co-authorship, citation, top authors, institutes, countries and source [26]. Performance analysis in the bibliometric was also used to review the approach to analyze the status and research trends of photocatalytic degradation of wastewater using TiO₂ with the keywords “doping”, “modification” and “heterojunction” [27]. Some other researchers use bibliometric analysis to review the chemical and physical methods to produce TiO₂, such as milling, microwave, sol-gel, hydrothermal, coprecipitation, pyrolysis and centrifugation [28] or using bibliometric analysis to review the application of heterogeneous photocatalysis to treat triclocarban and triclosan in greywater [29]. As such, this study satisfies the gaps in the TiO₂ modification strategies by providing a scientific mapping of the knowledge structure guided through the determined present and future trends. Addressing this research gap would strengthen efforts to modify and improve TiO₂ properties, potentially advancing large-scale wastewater treatment solutions. This study proposes bibliometric analysis for science mapping to reveal its knowledge structure.

The objectives of bibliometric analysis are to employ bibliographic coupling analysis to determine the current and emerging trends of TiO₂ modification techniques of wastewater through photocatalysis and to explore co-word analysis by investigating the future trends of TiO₂ modification approaches.

2. Methodology

2.1 Science mapping analysis

Bibliometric methodology is a statistical technique for performing science mapping analysis using bibliographic databases [30]. This analysis examines the degree of interconnection between various fields or disciplines using bibliometric databases such as Dimensions, PubMed, Scopus and Web of Science (WoS) [31]. By categorizing documents, authors, keywords, journals, institutions, and countries into distinct groups or clusters, this analysis delineates the structure of the research area. The analysis involved in this study is presented as follows:

- a) Bibliographic coupling evaluates the strength of the connection between two documents based on their shared references, revealing similarities in the research domain [32]. This analysis assesses the intellectual framework surrounding a particular topic [33]. By conducting this analysis, researchers can pinpoint recent developments that have yet to exert a significant impact [34].

- b) Co-occurrence profiling: This analysis examines how co-occurring terms in published works relate and proposes potential concepts depicted in the network [35]. According to [36], among all the bibliometric components, co-occurrence analysis is the sole technique that leverages the content of the publications to generate themes in a specific research area. Co-word analysis works in a way that it extracts the titles, abstracts and keywords of published works [37].

2.2 Research design and data collection

The filtering terms applied to filter publications connected by the relevant keywords are given in Table 1. The keywords are derived from the TiO₂ modification strategies in the context of wastewater application. The search “TS” option filters related articles from the preferred database system in WoS. The conference proceedings, book chapters, books, review papers and editorials are excluded from article selection. This step is crucial to ensure that the analysis produces high-quality results by reviewing only peer-reviewed journal publications.

Using a well-established and reputable database system like WoS, which enforces a rigorous peer-review process, confirming its high standard validation process [38]. Previous works have adopted identical approaches based on similar justifications [39,40]. VOSviewer version 1.6.20 was exercised in this work for the science mapping analysis.

The result of the bibliographic coupling analysis is illustrated as a network visualization in Figure 2. The clusters generated are distinct and independent from each other. All clusters are grouped closely. The current patterns and future development of TiO₂ are discussed for treating wastewater, including petrochemical, chemical and/or manufacturing effluents. By employing inductive interpretation and analyzing key articles within each cluster, the clusters were identified and synthesized based on their similar themes and research trends.

Table 1. The keywords used in the WoS database search.

No	Keywords	Justification
1.	“photocat*”	To search for the literature pertinent to photocatalysis
2.	“TiO ₂ ” OR “titanium dioxide”	To search for the literature pertinent to TiO ₂ as photocatalyst
3.	“modification” OR “dop*” OR “co-dop” OR “surface modif*” OR “composite form*” OR “morphological control” OR “hydrogenation” OR “deposit*” OR “defect” OR “defect engineering” OR “dye sensitiz*” OR “noble”	To search for the literature pertinent to modify TiO ₂
4.	“petrochemical” OR “chemical” OR “industrial” OR “manufacturing”	To search for the literature pertinent to types of wastewater that have been tested with photocatalysis process.
5.	“treatment” OR “degradation” OR “decomposition” OR “handling” OR “management”	To search for the literature pertinent to treatment of related wastewater

3. Findings and discussion

The query in WoS was conducted on 5 July 2024 and resulted in the final 898 articles after filtering exclusively for peer-reviewed article publications. The total citation number was 27,139 and the publications with no self-citations were reported as 26,735. With a 74 H-index, each document's mean score of citations was 30.46. The trend of citations versus the number of publications related to works on modifying TiO₂ for wastewater treatment is illustrated in Figure 1. An increasing trend over the years demonstrates a surge of interest from researchers owing to the need to alter the properties of TiO₂ as an alternative solution to the environmental problem. The citations and publications are expected to escalate in the future, contributing to the innovative and creative fabrication of TiO₂-based photocatalysts for effluent treatment.

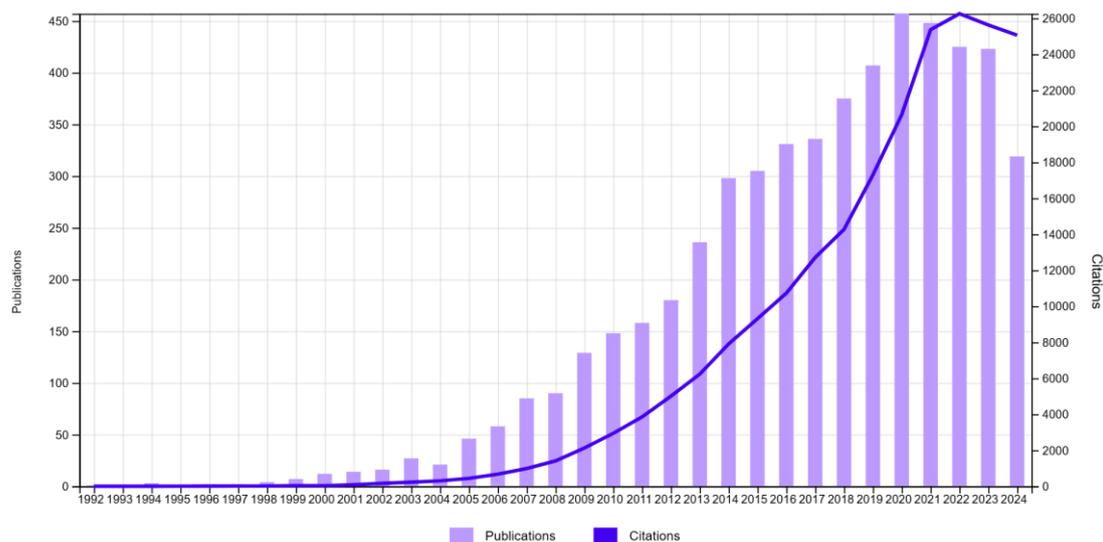


Figure 1. Number of citations and publications on TiO₂-modification strategies for wastewater treatment.

(Source: Web of Science)

3.1 Bibliographic coupling

With 898 retrieved documents, only 59 documents satisfy a threshold of 89 citations. The threshold was tested repeatedly to create the most vigorous network for a bibliographic coupling science map. The boundary was carefully chosen so too few articles would be displayed on the science map. On the other hand, a too low threshold will lead to under-filtering, hence forming irrelevant clusters in the map. The list of most cited articles, with the citation number and TLS from this analysis, is given in Table 2. The publication that recorded the highest TLS is identified to assess the strength of the bibliographic part. Articles with the highest TLS are [41] (82 TLS), [42] (74 TLS) and [43,44] (55 TLS). In this selection, the supposedly ranked first and third documents, [45] [46] were not considered as both review articles.

Table 2. The 10 leading journal articles in the bibliographic coupling analysis on TiO₂ modification approaches for wastewater treatment.

Rank	Publication	Citation	TLS
1.	Rafiq, A., Ikram, M., Ali, S., Niaz, F., Khan, M., Khan, Q., & Maqbool, M. (2021). Photocatalytic degradation of dyes using semiconductor photocatalysts to clean industrial water pollution. <i>Journal of Industrial and Engineering Chemistry</i> , 97(5), 111–128	520	82
2.	Dong, F., Guo S., Wang, Haiqiang., Li X., Wu Z., (2011). Enhancement of the Visible Light Photocatalytic Activity of C-Doped TiO ₂ Nanomaterials Prepared by a Green Synthetic Approach, <i>The Journal of Physical Chemistry C</i> , 115(27), 13285-13292	352	74
3.	Dong, F., Wang, H., Wu, Z., (2009). One-Step “Green” Synthetic Approach for Mesoporous C-Doped Titanium Dioxide with Efficient Visible Light Photocatalytic Activity, <i>J. Phys. Chem. C</i> , 113(38), 16717–16723	262	55
4.	Ren, W., Ai, Z., Jia F., Zhang, L., Fan, X., Zou Z., (2007). Low temperature preparation and visible light photocatalytic activity of mesoporous carbon-doped crystalline TiO ₂ , <i>Applied Catalysis B: Environmental</i> , 69(3) ,138-144	896	48
5.	Kuwahara, Y., Yamashita, H., (2009). Efficient photocatalytic degradation of organics diluted in water and air using TiO ₂ designed with zeolites and mesoporous silica materials, <i>J. Mater. Chem.</i> , 21(8) 2407-2416	100	45
6.	Huang Y., Ho, W., Ai, Z., Song, X., Zhang, L., Lee, S., (2009). Aerosol-assisted flow synthesis of B-doped, Ni-doped and B–Ni co-doped TiO ₂ solid and hollow microspheres for photocatalytic removal of NO, <i>Applied Catalysis B: Environmental</i> , 89(3), 398-405	106	42
7.	Wang, F., Li, F., Xu, M., Yu, H., Zhang, J., Xia, H., lang, J., (2015). Facile synthesis of a Ag(i)-doped coordination polymer with enhanced catalytic performance in the photodegradation of azo dyes in water, <i>J. Mater. Chem. A</i> , 3(11), 5908-5916	113	41
8.	Ajmal, A., Majeed, I., Malik, R.N., Iqbal, M., Nadeem, M. A., Hussain, I., Yousaf, S., Sheikh, Z.,Mustafa, G., Zafar, M. I., Nadeem, M., (2016). Photocatalytic degradation of textile dyes on Cu ₂ O-CuO/TiO ₂ anatase powders, <i>Journal of Environmental Chemical Engineering</i> , 4(2), 2138-214	100	38
9.	Qutub, N., Singh, P., Sabir, S., Suresh, S., Oh, W. C., (2022). Enhanced photocatalytic degradation of Acid Blue dye using CdS/TiO ₂ nanocomposite. <i>Sci Rep</i> 12(1), 5759	99	32
10.	“Uddin, M. T., Nicolas, Y., Olivier, C., Toupance, T., Muller, M. M., Kleebe, H. J., Rachut, K., Ziegler, J., Klein, A., Jaegermann, W., (2013). Preparation of RuO ₂ /TiO ₂ Mesoporous Heterostructures and Rationalization of Their Enhanced Photocatalytic Properties by Band Alignment Investigations, <i>The Journal of Physical Chemistry C</i> , 117(42), 22098-22110”	99	32

The result of the bibliographic coupling analysis is illustrated as a network visualization in Figure 2. The clusters generated are distinct and independent from each other. All clusters are grouped closely. The current patterns and future development of TiO₂ are discussed for treating wastewater, including petrochemical, chemical and/or manufacturing effluents. Using the induction interpretation and the analysis of the main articles in each cluster, the cluster was identified and synthesized based on the same subject and the trends of the representative research.

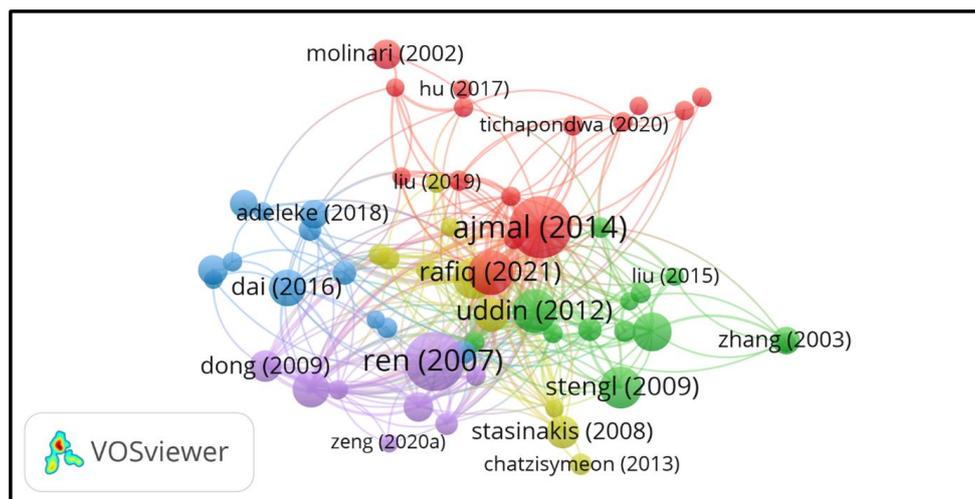


Figure 2. Bibliographic coupling on TiO₂ modification strategies for wastewater treatment

Cluster 1 (red): The total items appearing in the red cluster are 19 labelled “**copper-based dopant on TiO₂**”. The incorporation of impurity as the dopant in the lattice structure of TiO₂ was demonstrated to suppress the band gap and stretch the visible light wavelength [44]. The use of copper-based materials as a dopant to TiO₂ is widely investigated due to its capability to enhance charge isolation, visible light activation, creation of active sites, stability and durability, improved surface properties and catalytic synergy (acting as co-catalyst) [47]. Taking advantage of these virtues, [48] used simulated sunlight (UV-vis) and visible light to treat organic dyes over CuO/TiO₂ photochemically. It was found that both processes (sunlight and visible light) demonstrated non-uniform activity dependence upon CuO incorporation. However, The excessive CuO incorporation indicated an adverse effect due to the creation of recombination centres for the photogenerated carriers. The same nanocomposites, CuO/TiO₂, were used to degrade glycerol by reclaiming and reusing Cu [49]. From the phototreatment of glycerol, the experiment integrated with the H₂ production, implying the flexibility of CuO/TiO₂ as photocatalysts. Another work employing CuO was conducted to fabricate ternary nanocomposites, CuO/ZnO/graphitic carbon nitride (g-C₃N₄) [50]. This work achieved complete amoxicillin (AMOX) removal through a pH of 7 and catalyst loadings of 0.9 g/L in less than 120 minutes. The major radical responsible for the attack was verified to be hydroxyl via terephthalic acid photoluminescence (TPA-PL) spectroscopy.

Cluster 2 (green): Drawn from 13 publications, the label is determined as “**noble metal doped TiO₂ creating localized SPR**”. Gold deposition modifies the surface of nanocrystalline titania by creating a rough texture and increasing its surface area, which enhances the accelerated decomposition rate of wastewater [51]. It was found that the most advantageous surface concentration of gold nanoparticles for the Au/TiO₂ photocatalysts was 0.8 μgcm⁻², contributing to a 2-fold higher degradation

rate of methyl orange (MO) against pristine TiO₂ [52]. Another type of noble metal, Ag was commonly employed to alter the properties of TiO₂ via electrochemical methods. In the work published, Ag-Ag₂O/TiO₂ nanotube heterostructure indicated an intense visible light response and successful photogenerated carrier's separation and high adsorption capacity, leading to the nearly 100% higher than 17% and 13 % for acid orange 7 (AO7) and p-nitrophenol (pnp) over TiO₂ respectively, in less than 140 min [53]. Different noble metals, such as ruthenium, also used here RuO₂/TiO₂ were tested to photodegrade methylene blue (MB) by irradiating UV light [54]. From the XPS measurement, it is speculated that the band bending of 0.20 ± 0.05 eV may have caused a shift of Ti 2p_{3/2} core level spectra to low-end binding energy of 1.22 eV. The photoactivity of RuO₂/TiO₂ in degrading MB was twice as high as that of pure anatase TiO₂.

Cluster 3 (blue): Formed by 12 publications, the label of cluster 3 is determined as **“fabrication of graphene co-doping composite photocatalysts anchored on metal oxides”**. One of the works on the co-doping of graphene oxide (GO) with other components was conducted by synthesizing potassium (K), phosphorus (P) co-doped g-C₃N₄ (KPCN) and CoFe₂O₄ composite photocatalysts demonstrated 99% and 85% degradation rate of doxycycline and tetracycline antibiotics, respectively [55]. The co-doping strategy forms a heterojunction structure between KPCN and CoFe₂O₄ photocatalysts, enabling effective charge isolation. [56] attempted to fabricate MIL-53 (Fe)-rGO to treat Cr (VI) dyes using visible light. The enhanced MIL-53-rGO is reported through the electrostatic self-assembly strategy, where an interfacial contact between the rGO surface and MIL-53 (Fe) is effectively built, accelerating the photogenerated electron transfer.

Table 3. Bibliographic coupling analysis on TiO₂ modification strategies for wastewater treatment

Cluster no.	Cluster color	Cluster label	No. of publications	Representative article
1	red	Copper based dopant on TiO ₂	15	[65], [66], [67]
2	green	Nobel metal doped TiO ₂ creating localized surface plasmon resonance (SPR)	13	[82], [83], [84]
3	blue	Fabrication of graphene co-doping composite photocatalysts anchored on metal oxides	12	[65],[71], [72]

Table 3 provides an overview of the bibliographic coupling analysis, highlighting the identified clusters, associated colors, labels/themes, publication records, and key representative articles.

3.2 Co-occurrence analysis

The term co-occurrence was analyzed considering the author keyword analysis. Out of 3845 keywords, 56 keywords with high-frequency terms appeared and were selected as a popular statement in the context of TiO₂-modification approaches to treat wastewater, with a minimum citation of 27. The highest word occurrence is degradation (400, TLS=1787), followed by TiO₂ (343, TLS=1491) and

nanoparticles (221, TLS=1034). Table 4 presents the 15 most frequent keywords identified in the keyword co-occurrence analysis.

Table 4. Top 15 most frequent keywords found in the selected publications from the co-occurrence analysis on TiO₂ modification strategies for wastewater treatment.

Rank	Keyword	Occurrences	TLS
1.	Degradation	400	1787
2.	TiO ₂	343	1491
3.	Nanoparticles	221	1034
4.	Photocatalysis	220	963
5.	Oxidation	154	734
6.	Performance	143	718
7.	Removal	124	626
8.	Photodegradation	121	603
9.	Water	130	593
10.	Photocatalytic degradation	134	557
11.	Adsorption	100	495
12.	Photocatalyst	103	493
13.	Photocatalytic activity	103	469
14.	Doped TiO ₂	92	437
15.	TiO ₂	96	423

The network visualization of the mapping of the co-word analysis is depicted in Figure 3. The connected map indicates four different themes, formed by four distinct clusters, related to the other modification strategies of TiO₂ for enhanced wastewater treatment. The details of the primary clusters in the co-occurrence analysis are outlined below.

Cluster 1 (red): 19 keywords are grouped in this red cluster, which brings the theme of “**treating model pollutant via nanocomposites TiO₂**”. Nanocomposites-based TiO₂ have attracted significant interest in photocatalysis owing to their potential applications and exceptional properties in water treatment [57]. Composites like graphene, carbon nanotubes or polymers may enhance conductivity, charge separation and surface properties [58]. One of the examples of such a demonstration was carried out by utilizing the polyester coated by TiO₂/SiO₂ (1:0.5) nanocomposites to degrade 96.8% MB, determined by the digital image-based colorimetric (DIC) [59]. Another popular selection of nanocomposites is incorporating graphene into TiO₂ as single-walled carbon nanotubes (SWCNTs)/TiO₂. The work focuses on the near-complete removal of organic pollutants such as MB

and ciprofloxacin (CPF). It was claimed that the 98-99% degradation efficiency was achieved due to several factors such as surface groups ($\text{OH}\cdot$, $\text{O}_2\cdot^-$), low charge combination rate from CNT architecture and small crystallite sizes (7.2-10.4nm) [60]. An oxide form of graphene, which is graphene oxide (GO) is also utilized to form composite photocatalysts with TiO_2 , namely GO/TiO_2 . The photo-treated carcinogenic MB and malachite green (MG) were successfully carried out with 93 and 85% degradation within 13 and 60 minutes, respectively [61].

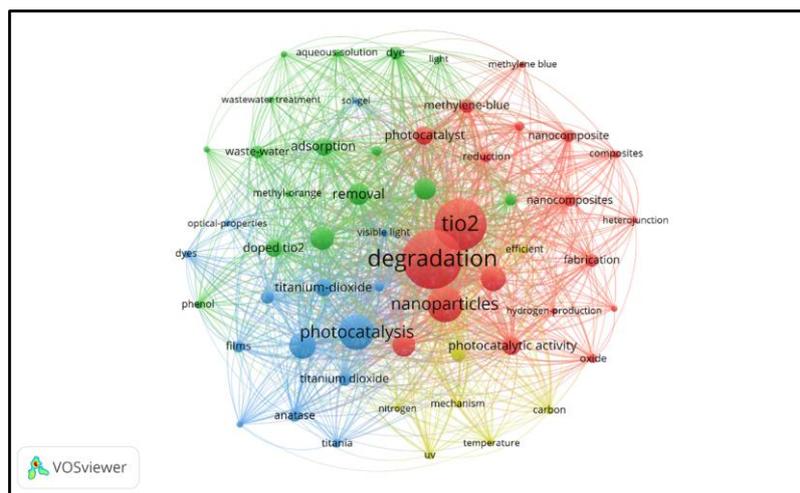


Figure 3. Co-word analysis on TiO_2 -modification strategies for wastewater treatment

Cluster 2 (green): This cluster includes 16 keywords with the theme “**Integration of advanced materials and processes such as adsorption and photocatalysis**”. It was discovered the optimized 1:2 mass ratio of graphite oxide (GO)/ TiO_2 brings about an improvement in the adsorption-photocatalytic treatment of MO and MB dyes with a degradation rate of 93.99% and 80.22%, respectively, after a treatment with UV light irradiation for 60 min [62]. High degradation performance was achieved compared to 1:1 and 2:1 (GO/ TiO_2 ratio) owing to the increased availability of sites for GO adsorption and TiO_2 electron-hole pair separation. Another recent article demonstrated a work on the fabrication of GO/TiO_2 with membranes, namely PVDF [63]. The adsorption test was carried out on the MB dyes for 30 mins before proceeding with the photocatalytic process. It was found that the PVDF/ TiO_2/GO indicated superior degradation efficiency, reaching 92%, higher than the removal of dyes using PVDF/ TiO_2 and PVDF/ ZnO . It was speculated that the abundance of oxygen-containing functional groups in GP creates effective electron traps, which capture the electrons generated by light and reduce the recombination of holes. This phenomenon results in efficient charge segregation. P25- TiO_2/N_2 -doped graphene quantum dots/reduced mildly oxidized graphene oxide (P25/NGQDs/r-GO), claimed to have been able to degrade MB, crystal violet (CV) and Basic Red 46 (BR46) to 96.6%, 100% and 82.4% respectively, due to the excellent synergistic effect of adsorption-photocatalytic property from NGQDs and GO, within 30 mins adsorption and 150 mins of photodegradation [64]. It was observed that the negatively charged NGQDs efficiently enhanced the adsorption capacity for positively charged dyes. Cluster 3 (blue): The third cluster is represented by 14 keywords. It explores the idea of “**harnessing the surface and optical properties of TiO_2 nanoparticles through thin-film deposition**”. Nanocatalyst films supply a vast surface-to-volume ratio that provides high adsorption [65] and reactive sites [66] of the target particles. Such innovation employed spin-coating technique to create N-doped TiO_2 films on glass substrates and studied the effect of doping using N_2 upon the optical

and photocatalytic process [67]. Due to N-doped coating, the absorption spectra of TiO₂ thin films shifted into the visible range. A coating approach using metal dopants such as Fe in TiO₂ thin films was conducted on the glass, silica rings and helixes [68]. The photodegradability of the Fe/TiO₂ thin layer was tested on the MO under sunlight. It was found that the Fe/TiO₂ thin film exhibits 2-2.5 times higher degradation capacity than the bare TiO₂ photocatalysts. Table 5 summarizes the main findings from the co-occurrence analysis, including cluster number and color, cluster labels, keyword count and representative keywords.

Table 5. Summary of co-word analysis on TiO₂-modification strategies for wastewater treatment.

Cluster Number and color	Cluster label	Number of keywords	Representative Keywords
1 (red)	Treating model pollutant via nanocomposites TiO ₂	19	Composites, methylene blue, nanocomposite, TiO ₂ , photocatalytic activity
2 (green)	Integration of advanced materials and processes; adsorption and photocatalysis	16	Adsorption, dyes, phenol, doped TiO ₂ , photodegradation
3 (blue)	Harnessing the optical and surface properties of anatase TiO ₂ nanoparticles through thin-film deposition.	14	Anatase, dyes, optical properties, oxidation, sol-gel, surface, thin films, TiO ₂

4. Implications

This study has underscored several implications for current and future trends in the modification techniques researchers employ worldwide to improve TiO₂ efficiency in wastewater treatment. From the bibliocoupling analysis conducted on the 898 documents, the current research trends focus on the main techniques: doping with transition metal oxides such as copper (Cluster 1) and noble metals (Cluster 2) and incorporation of composite materials such as graphene-based derivatives (Cluster 3) with TiO₂. Copper (Cu)-based dopants are one of the most commonly investigated dopants as they render the transformation of anatase to rutile during calcination, besides being cost-effective, non-toxic and efficient in absorbing a broad spectrum of solar light [69]. As compared to noble metals and transition metals such as Cu is relatively more available in resources [70]. A study compared the performance of gold, silver and copper-doped TiO₂ [71]. It was found that the photodecomposition of MB using TiO₂-based photocatalysts is in descending order: Cu/TiO₂ > Au/TiO₂ > Ag/TiO₂/ TiO₂. The XPS data indicated that the Ti³⁺ chemical state containing Cu nanoparticles for the TiO₂ thin films demonstrated the existence of the Ti₂O₃ phase on the surface, leading to the deficiency of O₂ on the surface and enriching superoxide, O₂⁻ anion hindering the e⁻-h⁺ recombination, resulting in the enhancement of 90% MB degradation in 60 minutes via Cu doping.

Apart from transition metal oxide and noble metal, graphene-based material is one of the trending research areas owing to its unique property of excellent conduct electric [72]. High electrical conductivity means the charge transfer between the photocatalyst and reactant may occur efficiently. Another distinguished property of graphene is the high specific surface area, which serves as an active sites for photocatalysis [73]. Other properties of graphene that attract the interest of researchers are

broad optical absorption, high mechanical strength, tunable electronic properties and high thermal conductivity [71]. In addition, the findings from co-occurrence analysis indicated a confluence with the results of the bibliographic coupling, where most of the works tend to explore and elevate the potential of advanced materials such as graphene-derived compounds. The selection of the form of graphene depends on the specific application, such as the need for high conductivity and the ability to absorb light efficiently [74].

5. Limitations

Several weaknesses can be found in this study, such as the inherent flaws of the bibliometric analysis method, which relies on the citation frequency. The citation count is impacted by other components, such as institutions and journal reputations. The sentiment is that low-ranked journals producing lower-quality articles may result in limited citations compared to more renowned journals and institutions. To maximize the inclusivity of the articles coverage, the bibliographic coupling analysis utilizes the total link strength (TLS) that represents the bibliographic strength of the published network. Moreover, the interpretation of results retrieved from Vosviewer software might be subjective, depending on the authors' deductive analysis, despite the objective and quantitative nature of the bibliometric analysis. As an alternative, several cognitive inputs were solicited from a single researcher to mitigate the introspective interpretation. In addition to that, the analysis relies solely on WoS, which may not comprehensively cover all relevant publications, especially non-English sources or regional sources or also known as database bias. However, the authors selected WoS on account of its stringent quality criteria that ensure the inclusion of peer-reviewed, credible and impactful research. WoS also has a well-established citation index, making it ideal for analyzing citation trends, co-occurrence networks and bibliographic coupling.

6. Future Research Avenues

There are several avenues for future research, such as the optimization of TiO₂ modification, leveraging novel doping strategies, including the use of rare earth materials as a third dopant to the existing binary photocatalyst; Cu/TiO₂, CuO/TiO₂, Cu₂O/TiO₂, GO/TiO₂, rGO/TiO₂. A recent work using different materials has shown that the ternary hybrid photocatalyst (SnS₂/BiOCl/BiOBr) presents a favorable stability and boosts the photocatalytic degradation rate to 220.5, 4.6 and 4.5 times higher than SnS₂, BiOCl and BiOBr respectively [75], via double S-scheme heterojunction construction. The finely produced nanoparticles SnS₂ were among the key successes in this work, as they generated a short electron path in that ternary heterojunction structure.

From the environmental point of view, researchers should consider a green chemistry approach to synthesize the ternary transition metal oxide (Cu, Fe, Cr, Ni, Co, Mn)/graphene/TiO₂-based photocatalysts. By employing the green chemistry principle, safer chemicals and processes are adopted, reducing harmful and hazardous chemicals to the environment [76]. Several works have been published to produce photocatalysts employing green chemistry, such as using aqueous extracts of *Moringa oleifera* for the fabrication of CuO/TiO₂ heterojunction [77]. Another work that used a green chemistry approach used an aqueous extract of lemongrass (*Cymbopogon citratus*), collected via the Soxhlet extraction to synthesize a binary compound Fe/TiO₂ [78]. There has been limited work on green chemistry-photocatalysis work, especially for the fabrication of ternary photocatalysts, which have proven more synergistic and efficient than single or binary photocatalysts [79–81].

7. Conclusion

This review has provided insight into current and future trends of the modification preference on the most widely investigated photocatalysts, TiO₂. This bibliometric analysis explicitly focuses on wastewater, encompassing textile, petrochemical and manufacturing effluent. From the bibliocoupling analysis of 898 docs, the current focus of the research area is on TiO₂ altering methods via doping with copper-based photocatalysts and composite formation using noble metal. Carbon-based materials such as graphene, GO, rGO have also been used to modify the surface of TiO₂. The co-occurrence analysis encompasses the direction of future research. The analysis indicates the tendency to use nanocomposites, advanced materials and integration of processes such as adsorption and optimizing the optical and surface properties of TiO₂ nanoparticles via thin film deposition.

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