Titanium dioxide photocatalyst: Present situation and future approaches

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Abstract: Over the past three decades, photocatalysis has evolved into a rapidly advancing research field, with titanium dioxide (TiO_2) established as one of its most robust and widely studied materials. Owing to its stability, non-toxicity, and strong oxidative potential, TiO_2 has become a very important component in environmental remediation technologies. This mini-review provides a concise overview of the key foundational studies that shaped our understanding of TiO_2-based photocatalysis, outlines the current state of commercially available TiO_2-enabled products and applications, and discusses critical directions and emerging challenges that will influence the future development of TiO_2 photocatalytic systems.

Keywords: Photocatalysis; Titanium dioxide; Water purification; Air purification

1. Introduction

Because of the importance of keeping our planet clean, researchers are actively working on alternative, eco-friendly technologies for all areas of daily life. Sustainable energy production and pollutant destruction are two areas in which intense research is being carried out. Photocatalysis semiconductor-mediated a well-established technique for pollutant degradation and hydrogen (clean fuel) production by water splitting. Photocatalysis can be defined as a “catalytic reaction involving the production of a catalyst by absorption of light” [1]. The appropriate positioning of valence (VB) and conduction (CB) bands makes them suitable materials for light absorption and photocatalytic action in semiconductors. Nanocrystalline titanium dioxide (NTO) is a multifunctional semiconductor photocatalyst that can be an environmental catalyst (in water and air purification), an energy catalyst (in water splitting to produce hydrogen fuel), or an electron transport medium in dye-sensitized solar cells [2]. NTO is unique in its chemical and biological inertness, photostability (i.e., not prone to photoanodic corrosion), and low cost of production compared to other available semiconductor photocatalysts [3]. Photocatalytic

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water and air purification using NTO is a widely used advanced oxidation process (AOP) because of its efficiency and eco-friendliness. The homogeneous photo-Fenton technique is another efficient AOP for the oxidation of water contaminants but requires the use of ferrous sulfate ($FeSO_4$) and hydrogen peroxide (H_2O_2)[4].

2. Structural characteristics

Titanium dioxide or titanium (IV) oxide, known as titania, with a molecular weight of 79.87 (g mol^{-1}), is titanium's naturally occurring oxide with the chemical formula TiO_2. It is named "Titanium White" and "Pigment White 6" when used as a pigment. Titanium dioxide is extracted from different naturally occurring ores containing ilmenite, rutile, anatase, and leucoxene, mined from deposits worldwide. In industry, the most significant part of titanium dioxide pigment is produced from titanium mineral concentrates by the so-called chloride or sulfate process, either as rutile or anatase form. The most fundamental Titanium White particles are typically between 200 and 300 nm in diameter, although larger aggregates and agglomerates are also formed [5].

Titanium dioxide (TiO_2) is used chiefly as a pigment in paints, sunscreens, ointments, and toothpaste. Titanium dioxide pigments are inorganic chemical products that impart whiteness, brightness, and opacity to various applications, including coatings, paper, plastics, and other industrial and consumer products. TiO_2 as a pigment derives value from its whitening properties and opacifying ability. As a result of TiO_2's high refractive index rating, it can provide more hiding power than any other commercially available white pigment [6]. Titanium dioxide crystals can exist in one of three crystalline forms: rutile, anatase, or brookite (Table 1). The basic building block in their structures consists of a titanium atom surrounded by six oxygen atoms in a more or less distorted octahedral configuration. In all three TiO_2 structures, the octahedra stack in threefold coordinated oxygen atoms.

Table 1. Crystallographic properties of rutile, anatase, and brookite [7]

Crystal structure	Density (g/cm^3)	System	Space group	Cell parameters (nm)		
				a	b	C
Rutil	4240	Tetragonal	D^{14}_{4h} – $P4_2/mnm$	0.4584	-	0.2953
Anatase	3830	Tetragonal	D^{19}_{4a} – $I4_1/amd$	0.3758	-	0.9514
Brookite	4170	Rhombohedral	D^{15}_{2h} – Pbca	0.9166	0.5436	0.5135

In these three TiO_2 crystals form, fundamental structural unit forms from TiO_6 octahedron units and have different modes of arrangement and links as presented in Fig. 1. In the rutile form, TiO_6 octahedra link by sharing an edge along the c-axis to form chains. These chains are then interlinked by sharing corner oxygen atoms to form a three-

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dimensional framework. Inversely in anatase, the three-dimensional framework is formed only by edge-shared bonding among TiO_6 octahedrons. More precisely, octahedra in anatase share four edges and are arranged in zigzag chains. In brookite, the octahedra share both edges and corners, forming an orthorhombic structure [8].

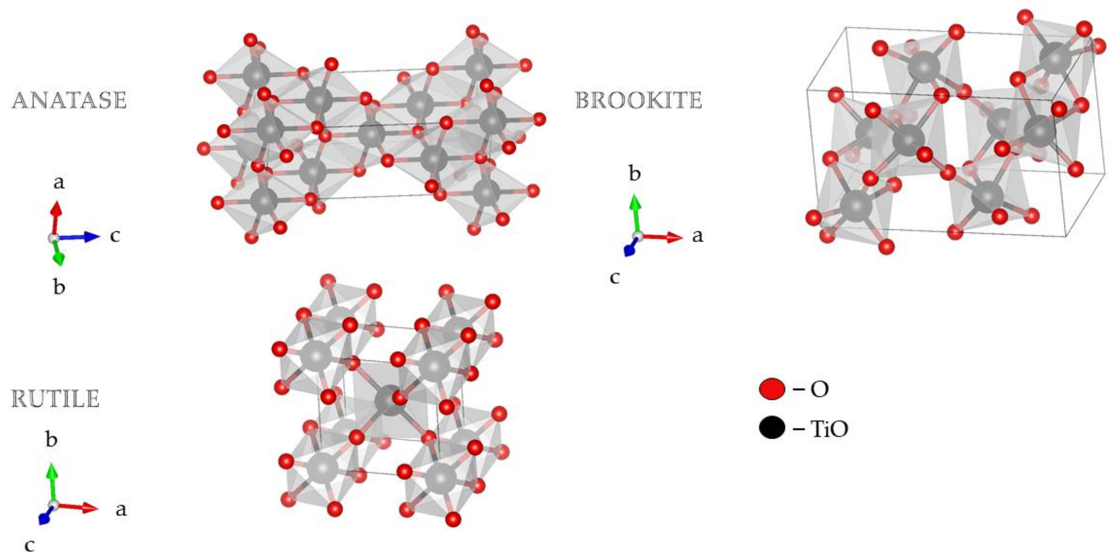

Figure 1. The crystalline structure of TiO_2 [9].

The X-ray diffraction (XRD) experimental method is used to design these crystal structures and evaluate the crystal grain size of anatase, rutile, and brookite, the X-ray diffraction (XRD) experimental method is used. Anatase peaks in X-ray diffraction have occurred at $\Theta = 12.65^\circ$, 18.9°, and 24.054°. The rutile peaks are found at $\Theta = 13.75^\circ$, 18.1°, and 27.2° while brookite peaks are encountered at $\Theta = 12.65^\circ$, 12.85°, 15.4°, and 18.1°. Θ represents the X-ray diffraction angle [10].

3. Present situation

As already mentioned, TiO_2 is a semiconductor that mineralizes many organic pollutants under UV radiation and has attracted the attention of many researchers thanks to its chemical stability, biocompatibility, and physical, optical, and electrical properties [11]. It has an extensive application. It is used in photocatalysis and processes that use light to activate a substrate because it facilitates the kinetics of a chemical reaction. It is suitable for converting toxic materials into harmless species [12].

It is most suitable for broad application in the field of environmental protection. It shows photocatalytic oxidation and photoinduced super hydrophilicity under UV light, making it a good candidate for photocatalytic materials and self-cleaning surfaces in air [13].

TiO_2 is widely used as a white pigment in the paint and food industry. In addition to being commercially available and non-toxic, it is very inexpensive. For the above reasons, it

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has attracted enormous attention for wastewater treatment. Due to its various applications and sound qualities, it possesses nowadays. A significant focus has been placed on it and its improvement in the future [14].

4. Future approaches

Titanium dioxide (TiO_2) is a photocatalyst widely accepted due to its non-toxicity, chemical inertness, high stability, and oxidation efficiency [15]. TiO_2 is a semiconductor that mineralizes many organic pollutants such as folate compounds, pesticides, herbicides, etc. Under UV radiation, that is, TiO_2 can use natural solar radiation in the near UV region [14].

Therefore, one of the biggest challenges in the future is to increase the spectral sensitivity of photocatalysts to visible light, which makes up the most significant part of solar radiation. To increase the efficiency of TiO_2 as a photocatalyst, using solar radiation and in natural conditions, the following are most often used coupling TiO_2 with photosensitizers and doping and modification of TiO_2. Doping the semiconductor material with suitable ions reduces the catalyst's energy gap and improves the photocatalytic efficiency in the visible radiation area. Doping the catalyst with metal ions (Fe, Mo, V, Ru, Rh, Mn, Cu) prevents the recombination of e^- - h^+ pairs so that the metal ions can serve as catchers of photogenerated electrons and holes. Previous investigations indicate that the photocatalytic activity of TiO_2 doped with a metal ion largely depends on the dopant's concentration. It is also possible to modify the surface of TiO_2 with metals such as Ag, Pt, Ni, and Cu, which also aims to reduce the recombination of e^--h^+ pairs, thus improving photocatalysis efficiency [14].

TiO_2 can also be coupled with semiconductors. Using two coupled semiconductors such as CdS/TiO_2 or Bi_2S_3 /TiO_2 having different energies of conduction and valence levels can lead to improvements in charge separation, prolong the charge carrier lifetime, and increase the efficiency of surface charge transfer to the adsorbed substrate [14].

5. Conclusions

Titanium dioxide has long been used to remediate organic substances present in wastewater. Consequently, significant effort has been directed during the last several years toward modifying this semiconductor material. In this review, we mentioned the various ways TiO_2 photocatalytic modifications are successfully utilized for the degradation of organic dyes, mainly aiming at high efficiency, activity in the visible range of the solar spectrum and effective catalyst reuse, etc. Modifications have been achieved using metals (noble metals, transition metals, lanthanide metals, alkaline, and alkaline earth metals, cadmium sulfide, etc.) and nonmetals (nitrogen, fluorine, sulfur, carbon, etc.).

In addition to the degradation of organic contaminants, the photocatalytic activity of TiO_2 has potential use as an additive in foods or medicines, electrodes of solar cells, etc. On

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the other hand, solar energy utilization is currently limited by the photo-inefficiency of the TiO_2 catalyst. Therefore, developing an innovative TiO_2 photocatalyst and its optimization is needed. This photocatalyst can be used commercially in photocatalytic water treatment technology.

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References

1. J.W. Verhoeven,Glossary of terms used in photochemistry. Pure and Applied Chemistry. 68 (1996) 2223–2286.
2. M. Pelaez, N.T. Nolan, S.C. Pillai, M.K. Seery, P. Falaras, A.G. Kontos, P.S.M. Dunlop, J.W.J. Hamilton, J.A., Byrne, K.A. O'Shea, A review on the visible light active titanium dioxide photocatalysts for environmental applications. Applied Catalysis B. 125 (2012) 331–349.
3. A. Mills, S. LeHunte, An overview of semiconductor photocatalysis. Journa of Photochemistry and Photobiology A. 108 (1997) 1–35.
4. G. Lofrano, L. Rizzo, M. Grassi, V. Belgiorno, V. Advanced oxidation of catechol: A comparison among photocatalysis, fenton and photo-fenton processes. Desalination. 249 (2009) 878–883.
5. K. Othmer, Encyclopadia of Chemical Technology, fourth edition, Wiley-Interscience Publication, 19 (1996).
6. H. Takeda, O. Ishitani, Development of efficient photocatalytic systems for CO_2 reduction using mononuclear and multinuclear metal complexes based on mechanistic studies. Coordination Chemistry Revews. 254 (2010) 346–354.
7. U. Diebold, The surface science of titanium dioxide. Surface Science Reports. 48 (2003) 53–229.
8. M. Yan, F. Chen, J. Zhang, M. Anpo, Preparation of Controllable Crystalline Titania and Study on the Photocatalytic Properties. The Journal of Physical Chemistry B. 109 (2005) 8673–8678.
9. S.J. Armaković, M.M. Savanović, S. Armaković, Titanium Dioxide as the Most Used Photocatalyst for Water Purification: An Overview. Catalysts 13 (2023) 26.
10. G.A. Mansoori, T.R. Bastami, A. Ahmadpour, Z. Eshaghi, Annu. Colloid-Mediated Transport and the Fate of Contaminants in Soils. Review Nano Research. 2 (2008) 439–494.
11. G.L. Puma, A. Bono, D. Krishnaiah, J.G. Collin, Preparation of titanium dioxide photocatalyst loaded onto activated carbon support using chemical vapor deposition: a review paper, Journal of Hazardous Materials. 157 (2008) 209.
12. C. McCullagh, N. Skillen, M. Adams, P.K.J. Robertson, Photocatalytic reactors for environmental remediation: a review. Journal of Chemical Technology & Biotechnology. 86 (2011) 1002–1017.
13. R.T. Sapkal, S.S. Shinde, T.R. Waghmode, S.P. Govindwar, K.Y. Rajpure, C.H. Bhosale, Photo-corrosion inhibition and photoactivity enhancement with tailored zinc oxide thin films. Journal of Photochemistry and Photobiology B: Biology. 110 (2012) 15–21.
14. S.J. Armaković, M.M. Savanović, S. Armaković, Titanium Dioxide as the Most Used Photocatalyst for Water Purification: An Overview. Catalysts. 13 (2023) 26.

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