



# Nonmetallic Mineral as the Carrier of TiO<sub>2</sub> Photocatalyst: A Review

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The composite photocatalyst can be constructed by using natural porous minerals with a wide range of sources, low prices and stable chemical properties as the titanium dioxide catalyst carrier, which can not only reduce the cost of catalyst preparation and application, but also effectively improve the dispersion, recyclability and catalytic performance of the catalyst. In recent years, a large number of scientific researchers have conducted a lot of research on the preparation and performance of porous mineral-supported composite catalytic materials. This paper describes the catalytic mechanism of titanium dioxide, as well as the research and application progress of various nonmetallic mineral materials supported by titanium dioxide, and prospects the development trend in the future.

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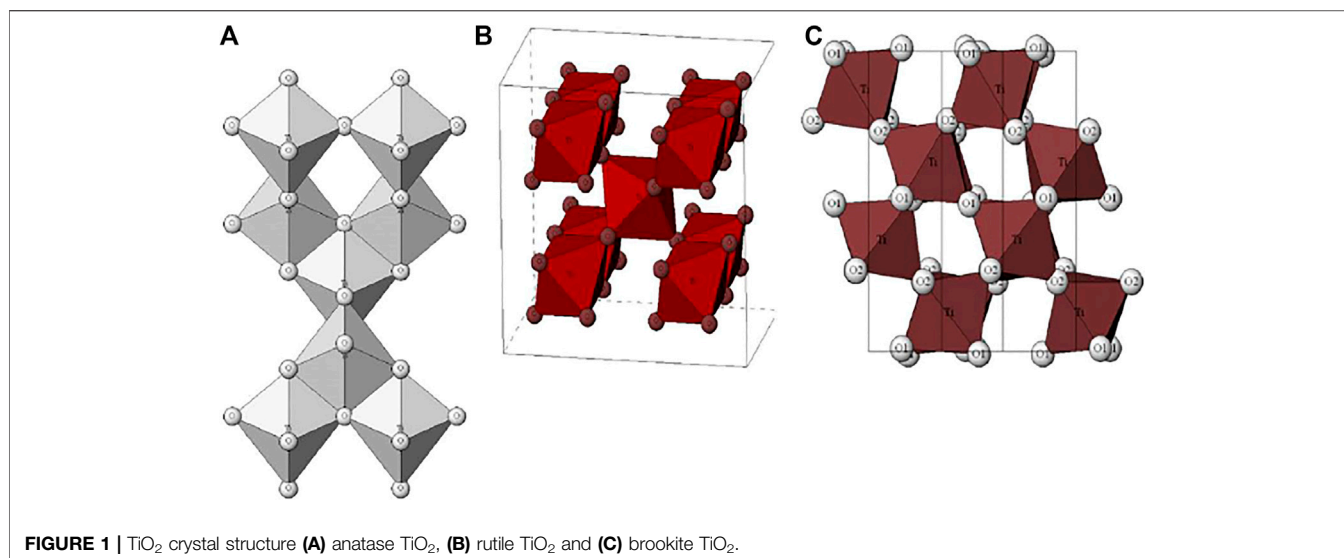
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## INTRODUCTION

With the rapid development of industry, environmental crises, which have blocked the further development of human civilization, is becoming more and more serious (Lin et al., 2019; Qiao et al., 2019; Xue et al., 2018). The use of photocatalytic technology in the advanced oxidation process is an effective method to solve the problem (Gaya and Abdullah 2007; Herrmann 1999). Photocatalytic technology evolves gradually developed in the 1970s. It is a technology that can convert solar energy into chemical energy to treat pollutants. In 1972, Fujishima and Honda discovered that titanium dioxide can split water to produce hydrogen when exposed to ultraviolet light (Fujishima and Honda 1972), which paved way for the research on semiconductor photocatalysis technology. Since then, semiconductor photocatalyst technology has been extensively researched, and it has been discovered that the technology can be used to split water for hydrogen evolution (Singh et al., 2014; Zhang et al., 2018; Li Shuang et al., 2021; Mohamed et al., 2021; Li Shuang et al., 2021), remove pollutants (Habibi et al., 2014; Frank and Bard 1977; Schrauzer and Guth 2002; Mastunaga 1985; Abdelraheem et al., 2019), reduce CO<sub>2</sub> (Li Kaining et al., 2021; Sun J et al., 2020; Yu et al., 2014; Low et al., 2017), Nitrogen Fixation (Wang et al., 2021; Wang et al., 2019; Wu et al., 2021). TiO<sub>2</sub> photocatalysis technology has been demonstrated to be an effective method for treating organic pollutants in both air and water (Tsoukleris D S et al., 2007; Singh T et al., 2021). It has the advantages of low cost, stable chemical properties, appropriate conduction band valence band potential, no secondary pollution, and low photo-corrosion, making it a research hotspot in the field of photocatalysis (Yan et al., 2019; Ding et al., 2019; Prakash et al., 2018; Selcuk S et al., 2018). However, several problems limit the applications of pure TiO<sub>2</sub>, including prone to agglomeration, Low specific surface area, difficulty recycling, high photogenerated electron-hole recombination rate, and limited light utilization wavelength range (Lavanya et al., 2014). It often requires immobilized load and visible light modification to improve its application performance. The crystal structure and morphology of TiO<sub>2</sub> are intended to improve the inherent optical properties, specific surface area, recycling problems, and charge transfer efficiencies, such as element doping (Akbarzadeh et al., 2010;



Ranganathan et al., 2016), compound semiconductors (Székely et al., 2021; Ding et al., 2019; Prakash et al., 2018; Selcuk et al., 2018), Nobel-metal deposition (Sato and White 1980; Gianmario 2000), and loading cocatalysts (Li Kaining et al., 2021; Ridhwan Samsudin et al., 2018). Among them, there are numerous types of research on loading cocatalysts, and the industrial application of photocatalysts can be realized by modifying the load.

Based on the rapid development of TiO<sub>2</sub>, we believe that it is necessary to summarize the carrier of TiO<sub>2</sub> photocatalyst and point out its development trend through further review. This article examines the most recent advances in titanium dioxide photocatalyst supports research and introduces the role of various nonmetallic mineral carriers. Furthermore, the photocatalytic performance improvement strategy and the use of titanium dioxide photocatalyst are summarized. Furthermore, we also discussed the current challenges facing TiO<sub>2</sub>-based composites as well as key issues that need to be resolved in future research. We hope that this review will provide a better understanding of TiO<sub>2</sub> and help solve its problems.

## PRINCIPLE OF TiO<sub>2</sub> PHOTOCATALYSIS

TiO<sub>2</sub> is an N-type semiconductor, and there are three main crystal structures: Anatase TiO<sub>2</sub>, Rutile TiO<sub>2</sub>, and Brookite TiO<sub>2</sub> (Hoffmann et al., 1995). The three crystal types are allotropes with each other, the most fundamental crystal structure unit is the same, composed of titanium oxide octahedron [TiO<sub>6</sub>], and the crystal structure of the three crystals is shown in **Figure 1** (Pelaez et al., 2012). When compared to the rutile phase, anatase phase TiO<sub>2</sub> demonstrated greater photocatalytic activity for the degradation of all substances (Lavanya et al., 2014). The higher photocatalytic activity in anatase TiO<sub>2</sub> is attributed to parameters such as the band-gap, number of hydroxyl groups, surface area, and porosity of the catalyst (Tayade et al., 2007). Anatase titanium dioxide has a strong ability to adsorb and

capture oxygen, and has a large specific surface area. Its electrons and holes are difficult to recombine, so its activity is high. Meanwhile, studies have shown that the particle size of titanium dioxide has a decisive effect on the stability of the crystal phase (Song et al., 2021; Lee et al., 2019; Gong and Selloni 2005).

When TiO<sub>2</sub> is illuminated with an energy greater than or equal to its forbidden bandwidth (for anatase TiO<sub>2</sub>, it must receive light with a wavelength less than 387.5 nm, limiting the use of photocatalysts), the electrons on the valence band are excited and undergo transition. When transferred to the conduction band, the photogenerated electron (e<sup>-</sup>)-hole (h<sup>+</sup>) pairs are separated, and such photogenerated electron (e<sup>-</sup>)-hole (h<sup>+</sup>) pairs are collectively called carriers. One of these photogenerated carriers will recombine within a few picoseconds (ps), while the other will migrate to the surface of TiO<sub>2</sub> within a few nanoseconds (ns) to immediately undergo redox reactions and react with oxygen and water to form highly active oxides (Tachikawa et al., 2007), oxidize substances that do not react with light into hydroxyl radicals (·OH), while photogenerated electrons will generate strong reducing superoxide radicals (·O<sub>2</sub><sup>-</sup>) in the redox reaction. (·OH) has strong oxidizing properties, which can destroy carbon-carbon bonds (C—C), carbon-hydrogen bonds (C—H), carbon-nitrogen bonds (C—N), and carbon-oxygen bonds (C—O) in organic matter. Nitrogen-hydrogen bonds (N—H), for example, eventually degrade organic pollutants into CO<sub>2</sub>, H<sub>2</sub>O, and other simple inorganic substances that can be emitted (Gaya and Abdullah, 2008). Because of the presence of hydroxyl radicals and superoxide radicals, the general redox reaction produces intermediate products but does not stop there, resulting in no intermediate products remaining in the reaction. The reaction mechanism of titanium dioxide photocatalyst is shown in **Figure 2** (Pelaez et al., 2012).

The specific reaction equation of the titanium dioxide photocatalyst is:

When TiO<sub>2</sub> is exposed to light with a wavelength of less than 387.5 nm, it generates photo-generated electrons and holes:

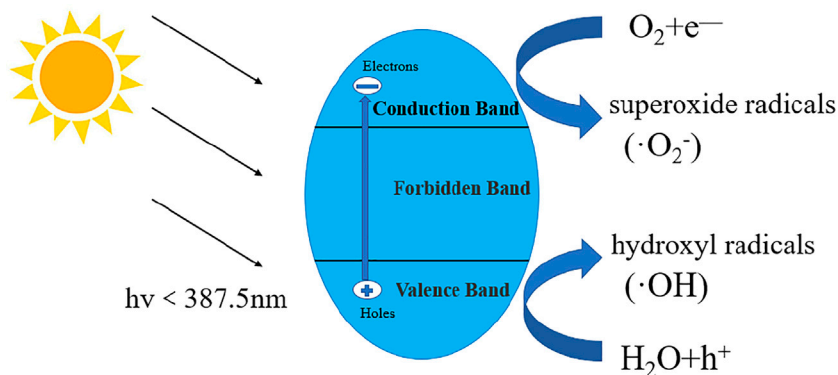


FIGURE 2 | Reaction principle diagram of titanium dioxide catalyst

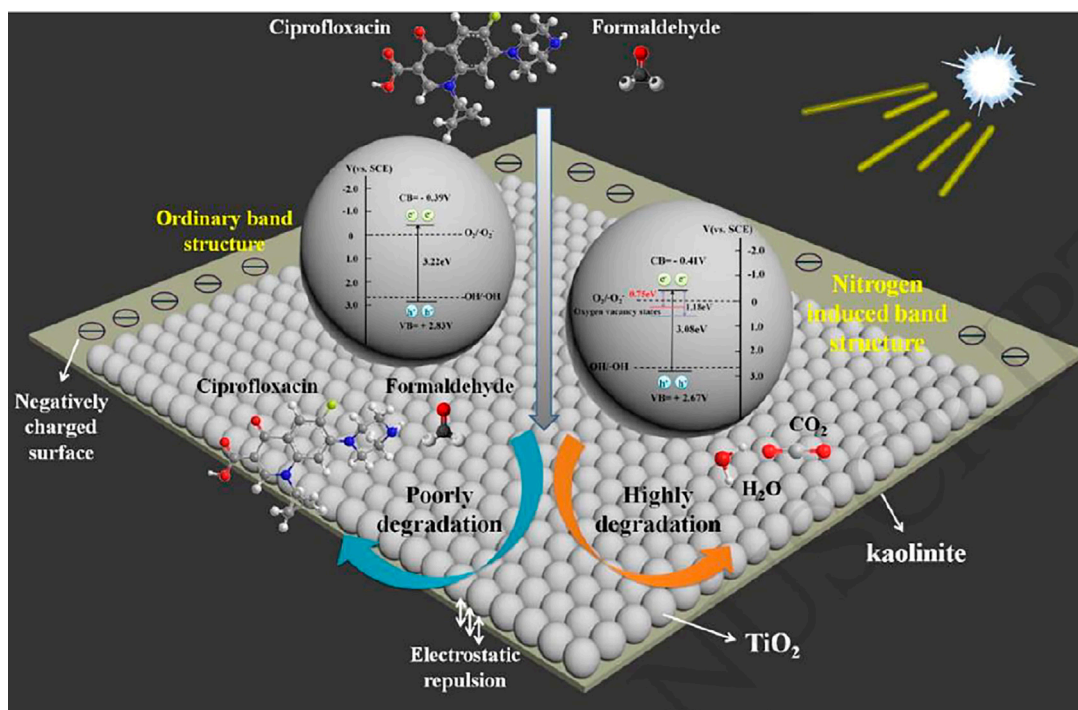
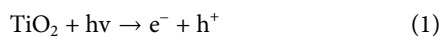
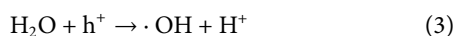


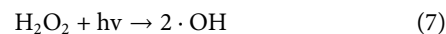
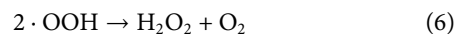
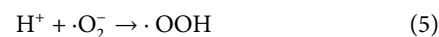
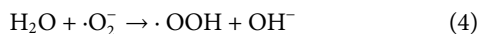
FIGURE 3 | The diagram description of the photocatalytic degradation enhancement mechanism of  $\text{TiO}_2/\text{kaolinite}$  composite (Li et al., 2018b).



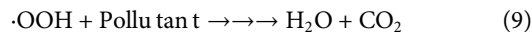
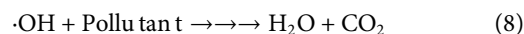
Superoxide radicals ( $\cdot\text{O}_2^-$ ) and hydroxyl radicals ( $\cdot\text{OH}$ ) are generated on the conduction band and valence band respectively:

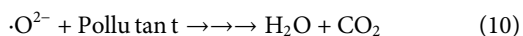
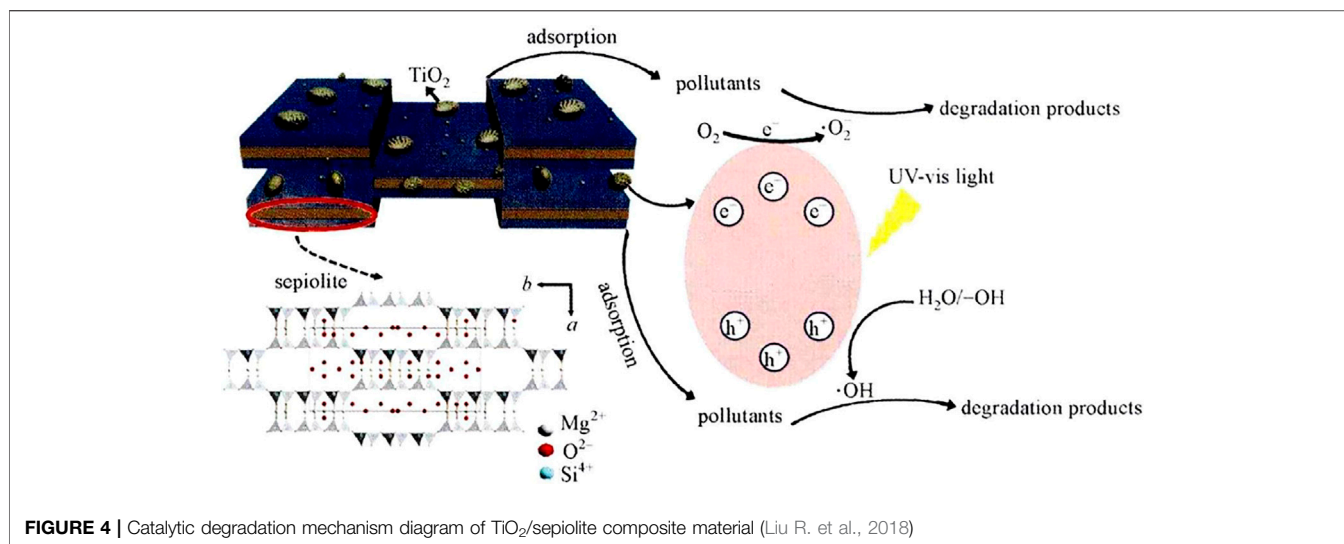


The generated superoxide radicals ( $\cdot\text{O}_2^-$ ) and hydroxyl radicals ( $\cdot\text{OH}$ ) will react with  $\text{O}_2$ ,  $\text{H}_2\text{O}$  and other groups to produce strong oxidizing free radicals ( $\cdot\text{OOH}$ ) and  $\text{H}_2\text{O}_2$ :



These radical groups with strong redox properties can indiscriminately oxidize the pollutants adsorbed on the surface of titanium dioxide into non-toxic water, carbon dioxide and other simple inorganic substances:





The method of preparing TiO<sub>2</sub> can be roughly divided into three methods: gas phase method, liquid phase method, and solid phase method, including sol-gel method (Dikici et al., 2018; Shimelis et al., 2017), hydrolysis precipitation method (Zhu et al., 2019), hydrothermal method, immersion method, mechanochemical method, microemulsion method, Magnetron sputtering method, etc.

## NON-METALLIC MINERALS SUPPORTED TiO<sub>2</sub>

In the process of using TiO<sub>2</sub> photocatalyst, to improve the photocatalytic activity, the photocatalyst is often made into nano-powder to increase the specific surface area of the powder and increase the number of photocatalytic active sites (Shi et al., 2009). When powder TiO<sub>2</sub> is used directly as a functional material for water treatment, however, defects such as easy agglomeration and recovery difficulty limit its application in advanced wastewater treatment (Kumar and Devi 2011). Rong Wang et al. discovered that when nano-TiO<sub>2</sub> comes into contact with water, it will produce a highly hydrophilic and lipophilic surface when exposed to ultraviolet light, and the contact angle quickly approaches 0° (Wang et al., 1997).

According to research, the grain size of titanium dioxide has a direct impact on its photocatalytic performance (Song et al., 2021; Lee et al., 2019). The photocatalytic degradation rate of anatase TiO<sub>2</sub> nanoparticles increased significantly when the grain size was increased from 6.6 to 26.6 nm (Wang et al., 2014). The photo-reactivity was found to increase with increasing crystallite size but to be independent of the crystallinity. The shape of the primary particles can also have a significant impact on titania nanoparticles' photocatalytic activity. Compared to spherical, cubic or hexagonal shapes have better photocatalytic activity. (Scotti et al., 2009). After TiO<sub>2</sub> is loaded on a suitable carrier, it

can avoid the agglomeration of nano-TiO<sub>2</sub> particles, and solve the problem of difficulty in separating titanium dioxide from liquid, and will not cause secondary pollution. Simultaneously, the loaded TiO<sub>2</sub> can achieve a larger specific surface area and adsorption performance, realize pollutant enrichment on the carrier's surface, and increase the possibility of contact between the photocatalyst and organic pollutants, thereby improving TiO<sub>2</sub>'s photocatalytic efficiency. As a photocatalytic carrier, non-metallic minerals have the following advantages: wide sources, low price, stable chemical properties, and natural porous structure. After loading photocatalyst, it can not only reduce the cost of preparation and application of composite photocatalyst, but also improve the dispersion, recoverability and catalytic performance of photocatalyst. Teh C M's research shows that a higher specific surface area can promote the adsorption of more reactant molecules to the surface of the catalyst, thereby avoiding the recombination of photogenerated electron-hole pairs (Teh and Mohamed 2011). **Table 1** shows the research progress of TiO<sub>2</sub>/non-metallic mineral composite photocatalytic materials in the treatment of pollutants. (Unless otherwise specified, it is the contaminants in the treatment solution).

## LAYERED SILICATE MINERAL KAOLINITE SUPPORTED NANO-TiO<sub>2</sub>

Kaolin is a kind of aluminum-containing layered silicate mineral. Its structural unit layer is made up of a 1:1 structural unit layer of silicon-oxygen tetrahedral sheets and aluminum-oxygen octahedral sheets (Vimonses et al., 2010). The calcination of kaolin is a dehydroxylation and aluminum activation process, and the crystal structure changes from layered kaolinite to amorphous metakaolinite at the same time. Kaolinite as a TiO<sub>2</sub> photocatalyst carrier can improve the agglomeration of nano-TiO<sub>2</sub> particles on the one hand, and realize the uniform loading of nano-TiO<sub>2</sub> particles on the surface of kaolinite (Li CQ,

**TABLE 1** | Research progress of TiO<sub>2</sub>/non-metallic mineral composite photocatalytic materials in the treatment of pollutant.

Photocatalyst	Light source	Photocatalyst concentration	Pollutants photocatalytic	Photocatalytic degradation activity	Reference
2N-3Fe-TiO <sub>2</sub> /X zeolite	visible light (5 W, λ > 420)	TiO <sub>2</sub> /Ze in the catalyst were 3.5 and 7% 0.013 g of catalyst	acetaldehyde(1000 ppm in air)	47%, which is 2.1-fold that of unmodified pure TiO <sub>2</sub> paper	Izadyar and Fatemi (2013)
TiO <sub>2</sub> /hydrophobic zeolite	irradiation (λ > 350 nm, 252 W)	weight ratio of TiO <sub>2</sub> /zeolite at 1/2	Formaldehyde (90 ppm in air)	Completely remove (80 h)	Zhu et al. (2018)
TiO <sub>2</sub> /zeolite	UV lamp (λ = 254 nm, 21 W)	0.1 g catalyst	methyl orange (100 ml 10 ppm)	45% (6 h)	Zhao et al. (2018)
TiO <sub>2</sub> /The natural zeolite	UV lamps (365 nm, 40 W)	0.1 g catalyst	100 ml 10 ppm of RhB, MO and HCHO	degrade RhB to 92.3% after 45 min degrade MO to 77.3% after 45 min degrade HCHO to 66.3% after 240 min	Zhang et al. (2018)
TiO <sub>2</sub> /zeolite	UV-light irradiation (365 nm)		crystal violet (150 ml 25 ppm)	99.96% (210 min)	Cherrak et al. (2020)
TiO <sub>2</sub> /ZSM-5 zeolite	8 W Philips 6.5 mW cm <sup>-2</sup> irradiance	30 mg catalyst	Formaldehyde(15 ppm in air) trichloroethylene(25 ppm in air)	900 ml/min of formaldehyde 700 ml/min of trichloroethylene	S. Suárez et al., 2018
TiO <sub>2</sub> /sepiolite	A 300 W Xe lamp	0.8 g/L	Orange G (150 ml 10 mg/L)	80% (60 min)	Zhou et al. (2018)
Mn-TiO <sub>2</sub> /sepiolite	visible lamp (23 W)	25 mg photocatalyst	emerald green (50 ml 50 mg/L)	98.13% (120 min)	Zhu et al. (2020)
TiO <sub>2</sub> /sepiolite	UV-vis light (350 nm ≤ λ ≤ 780 nm)	1 mg per 1.0 ml of catalysts	20 mg/L of MO or MB	degrade methyl orange to 90.7% after 70 min degrade methylene blue to 97.8% after 50 min	Liu et al. (2018a)
TiO <sub>2</sub> /kaolinite	20 W UV lamp (λ = 253.7 nm)	0.15 g catalyst	acid red G (100 ml 30–50 mg/L)	68% (10 min in dark) Completely remove (90min)	Zhang et al., 2011a
TiO <sub>2</sub> /kaolinite	20 W UV lamp (λ = 253.7 nm)	0.15 g catalyst	4-nitrophenol (100 ml 0.5 g/L)	90% (240 min)	Zhang et al., 2011a
TiO <sub>2</sub> /kaolinite	a germicidal lamp (Philips PL-S 9W, NL)	0.125 g of catalyst (0.25 g/L)	orange II (100 ml 10 mg/L)	nearly 100% (120 min)	W. Hajjaji et al., 2016
TiO <sub>2</sub> /kaolinite	500 W Xe lamp	0.1 g catalyst	ciprofloxacin (100 ml 10 ppm)	92% (45 min)	Li et al., 2018a
Fe-doped TiO <sub>2</sub> /Kaolinite	LED (50 W)	5.0 mg/ml	bacterial inoculums of Escherich (1.3*10 <sup>9</sup> )	inhibited the <i>Escherichia coli</i> 98% (120min)	Aritonang, et al., 2021
TiO <sub>2</sub> /diatomite	UV lamps (λ = 365 nm)	1.0 g on the glass plate (50 cm × 50 cm)	Formaldehyde (0.974 ± 0.05 mg/m <sup>3</sup> in air)	90.9% (180 min) higher than pure TiO <sub>2</sub> (80.3%)	Zhang et al. (2017)
TiO <sub>2</sub> /diatomite	150 W Xenon lamp (with a filter to screen out UV light)	the ratio of catalyst to TC solution was 5 g/L	tibiotic tetracycline (10 mg/L)	92% (150 min)	Chen et al. (2021)
TiO <sub>2</sub> /diatomite	UVA lamps (8 W, 365 nm)	1.0 g of the composite	Acetone or p-xylene (10 ppm in air)	total organic carbon degradation rate 25.8% (the light intensity was 0.48 mW/cm <sup>2</sup> ) 52.5% (the light intensity was 0.78 mW/cm <sup>2</sup> , the same as 1.33 mW/cm <sup>2</sup> )	Zhang et al. (2020)

2018). On the other hand, the highly temporary surface is densely concentrated with negatively charged hydroxyl groups, which can promote carrier separation and improve quantum efficiency. **Figure 3** shows the diagram description of the photocatalytic degradation enhancement mechanism of TiO<sub>2</sub>/kaolinite composite (Li et al., 2018b).

Hongliang Xu et al. prepared the kaolinite/TiO<sub>2</sub> composite material by the sol-gel method. The results show that intercalation and exfoliation reduce the size and thickness of the kaolinite particles. The acid treatment improves the distribution and loading of TiO<sub>2</sub> crystal grains. Both acid treatment and kaolinite exfoliation improved the photocatalytic performance of the kaolinite/TiO<sub>2</sub> composite photocatalyst, but the acid treatment is more conducive to the preparation of high performance kaolinite/TiO<sub>2</sub> composite

photocatalyst than exfoliation (Xu et al., 2018). Zhang Y et al. generated TiO<sub>2</sub>/Kaolin composite photocatalytic material with mixed crystal composition, and the specific surface area of the composite material reached 113.5 m<sup>2</sup>/g, demonstrating excellent removal effect on acid red G and p-nitrophenol under UV irradiation (Zhang et al., 2011a). Kibanova D et al. prepared TiO<sub>2</sub>/kaolin and TiO<sub>2</sub>/montmorillonite composite photocatalysts, respectively, to study the removal effect of gaseous formaldehyde under different light sources and humidity conditions, and compared them to Degussa P25 photocatalyst. It was found that the removal rate under UVA (365 nm) irradiation was not as high as that under UVC irradiation. When the humidity is 10% in the same light source, the removal effect of pollutants is optimal, but too much humidity results in a lower removal rate (Kibanova

et al., 2009). Wang C et al. formed a TiO<sub>2</sub>/Kaolin nano-photocatalyst via titanium tetrachloride hydrolysis. The experimental results show that kaolin promotes anatase formation while inhibiting anatase transformation to rutile. Ti-O-Si bond is formed in the composite material. The sample calcined at 200°C has the smallest grain size and an abundance of oxygen vacancies and defects on the surface, which can significantly reduce the composite efficiency of electron-hole pairs (Wang et al., 2011). Tokarský J et al. used hydrolytic precipitation to construct a TiO<sub>2</sub>/kaolinite composite photocatalytic material from titanium sulfate. Kaolinite could be converted into metakaolinite by forging and burning at 600°C, and TiO<sub>2</sub> nanoparticles on the surface of kaolinite were found to be in order by simulation with the empirical atomic field. As the target pollutant, acid orange 7 aqueous solutions were used. It degrades effectively. After urea intercalation and heat treatment (Tokarský et al., 2012). Matějka V et al. produced flake kaolinite. After the kaolinite was peeled off, the specific surface area increased from 14 to 24 m<sup>2</sup>/g. TiO<sub>2</sub> particles were immobilized on the surface of kaolinite by titanium sulfate was used as a titanium source, and azo dye acid orange 7 was desorbed under UV light. It is found that the composite was discovered to have high photocatalytic activity (Matějka and Neuwirthová 2014). Kočí K et al. prepared TiO<sub>2</sub>/kaolinite composite by hydrolyzing precipitation of titanium sulfate. When applied to the photocatalytic reduction of CO<sub>2</sub>, it was discovered that the composite produced more methane and methanol than commercial P25 (Kočí et al., 2011). Zhang Y et al. prepared TiO<sub>2</sub>/Kaolinite composite by low-temperature hydrolysis precipitation method. Anatase and rutile phases, titanite and rutile phases, and a mixed phase of anatase, titanite, and rutile coexisted in the TiO<sub>2</sub>/Kaolinite composite. At 700°C, the composite degraded acid red G and p-nitrophenol immensely well (Zhang et al., 2011a).

## CHAIN SILICATE MINERAL SEPIOLITE LOADED WITH TiO<sub>2</sub>

Sepiolite is a kind of magnesium-containing porous chain silicate mineral. It has a chain-like and layered transition-type structure in its crystal structure. Two layers of silicon-oxygen tetrahedra are joined by magnesia octahedra. Because of its abundant acid-base center, large specific surface area, and high mechanical strength, sepiolite is widely used in catalysis (De la Caillerie and Fripiat 1992). **Figure 4** shows the catalytic degradation mechanism diagram of TiO<sub>2</sub>/sepiolite composite material (Liu et al., 2018a).

Li et al. prepared a magnetic TiO<sub>2</sub>/sepiolite photocatalytic composite material by the sol-gel method, which has an outstanding synergistic degradation effect on pentavalent chromium ions and dichlorophenol (Li et al., 2015). Zhang et al. synthesized a kind of TiO<sub>2</sub> supported acid-activated sepiolite fibers under low-temperature conditions. They discovered that the specific surface area of the composite material was significantly greater than that of the original sepiolite and that the photocatalytic activity of the TiO<sub>2</sub>/AAS composites is excellent and superior to that of the TiO<sub>2</sub>/sepiolite

(raw sepiolite) and pure TiO<sub>2</sub>. The addition of sepiolite significantly improves the photocatalytic activity of titanium dioxide (Zhang et al., 2014; Zhang et al., 2011b).

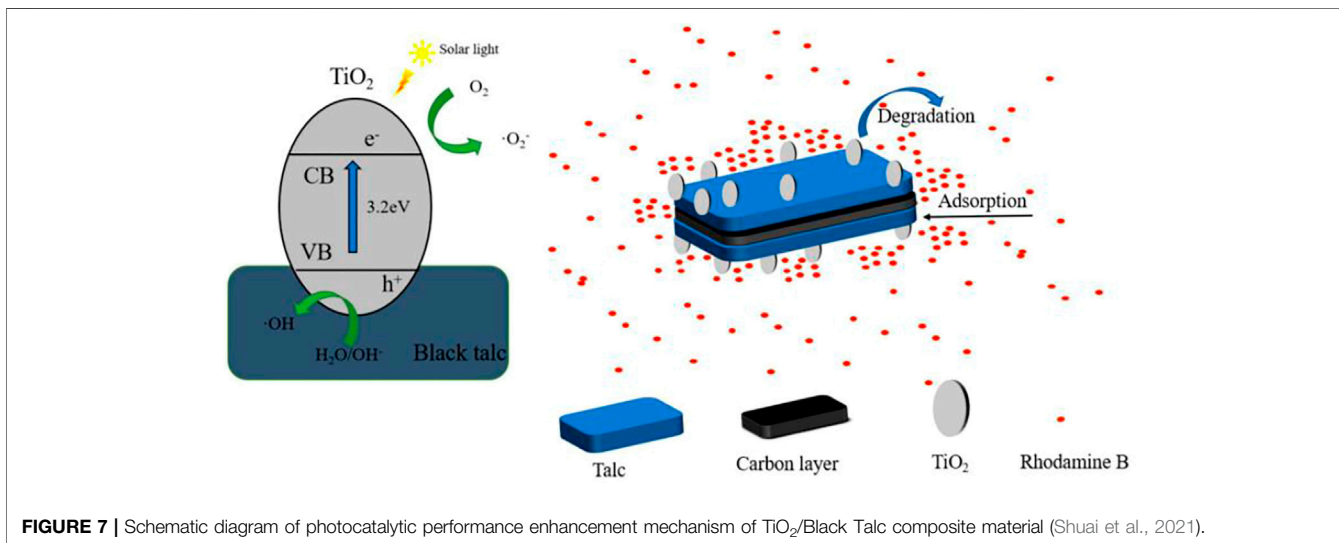
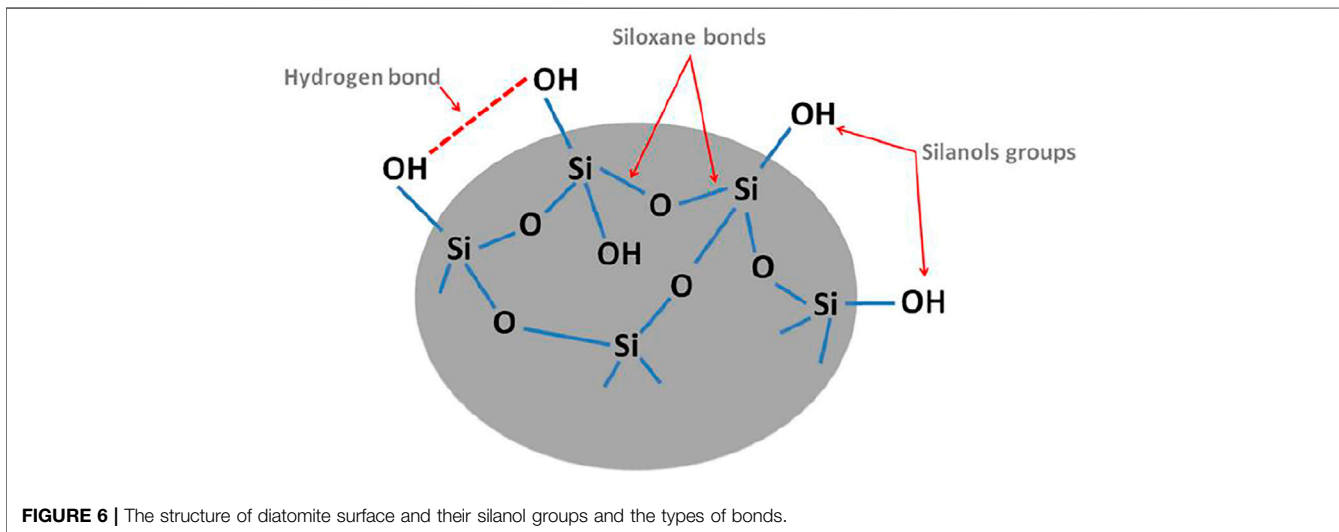
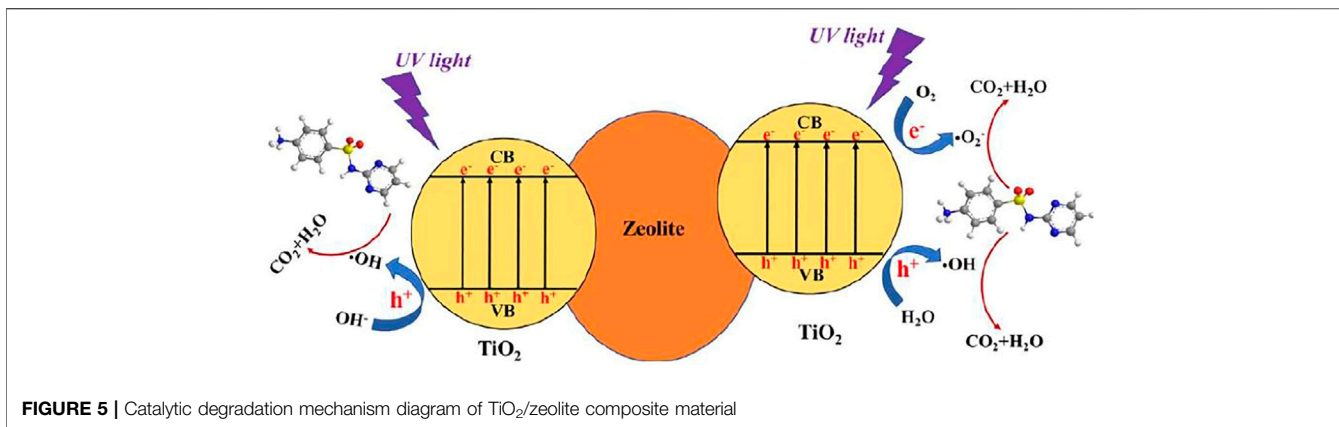
Uğurlu M et al. synthesized a TiO<sub>2</sub>/sepiolite composite photocatalyst using sepiolite as a carrier, which has a good photocatalytic effect on phenol and lignin and investigated the pH value of the solution. The effect of the amount of catalyst and temperature on photocatalytic performance. The findings of this study show that using sepiolite as a carrier can raise the crystal transition temperature of TiO<sub>2</sub> and inhibit crystal grain growth and agglomeration, and that sepiolite adsorption can promote the deep progress of a photocatalytic reaction. Zhang et al. used titanium tetrachloride as the titanium source and prepared an Au-doped nano-TiO<sub>2</sub>/sepiolite composite photocatalytic powder material by the sol-gel method. Methyl orange and Congo red have good degradation properties (Uğurlu and Karaoğlu 2011). Zhang D et al. used the microwave hydrothermal method to load TiO<sub>2</sub> onto the surface of sepiolite fiber, with the anionic dye orange G serving as the target degradation product. The catalytic results revealed that the obtained composite material has a high specific surface area. It is distributed on the surface and has a good degradation effect on orange G (Zhang 2014).

## RACK-SHAPED SILICATE MINERAL ZEOLITE LOADED WITH TiO<sub>2</sub>

A zeolite is a group of water-containing alkali metal and alkaline earth metal framework aluminosilicate minerals. The zeolite crystal lattice contains a large number of uniformly sized pores and channels. The pores are connected by open channels that allow them to communicate with the outside world. At the same time, these channels are easily occupied by Na, Ca, K, and other cations and water molecules. Among all TiO<sub>2</sub> supporting carriers, the zeolite molecular sieve has the largest specific surface area, the most irregular inner surface layout, the highest chemical stability, the best particle exchange performance, and the ability to provide a unique nano-scale reaction field. It is widely used in the support of TiO<sub>2</sub> photocatalysts. The supported zeolite molecular sieve can enrich the low-dose organic substrates in the liquid system on the surface of the catalyst and catalyze the concentrated catalysis, and increase the degradation rate of organic pollutants (Su et al., 2017; Yener et al., 2017).

Liu X et al. used a sol-gel method to generate a TiO<sub>2</sub>/zeolite (TiO<sub>2</sub> loaded amount of 30%) composite material and investigated its adsorption and photocatalytic degradation performance for sulfadiazine (SDZ) under ultraviolet light irradiation. The results show that under neutral pH conditions, the TiO<sub>2</sub>/zeolite sample can remove % of SDZ in 120 min. It is because the synergistic effect of TiO<sub>2</sub> photocatalyst and zeolite adsorbent in the composite material accelerates the photodegradation rate of SDZ in water. **Figure 5** shows the catalytic degradation mechanism of TiO<sub>2</sub>/zeolite composite material (Liu X. et al., 2018).

Similarly, Kovalevskiy N S et al. studied the photocatalytic degradation efficiency of TiO<sub>2</sub>/zeolite composite materials for various VOCs was investigated, and it was discovered that TiO<sub>2</sub>/



zeolite composite materials can inhibit secondary pollution and improve air purification efficiency when compared to pure  $\text{TiO}_2$  (Kovalevskiy et al., 2018). Zhang G et al. prepared a  $\text{TiO}_2$ /zeolite composite material by a hydrolysis deposition method and chose formaldehyde and organic dyes in water (phenol, MO, and RhB) as target degradation products to study the material's photocatalytic activity. The findings show that, when compared to pure  $\text{TiO}_2$ , the  $\text{TiO}_2$ /zeolite composite material has higher photocatalytic degradation activity and a higher degradation efficiency for organic pollutants (Zhang et al., 2018).

There are many types of zeolite molecular sieves used to support  $\text{TiO}_2$  photocatalysts. Different types of zeolite molecular sieves have different structures and properties, and their effects on  $\text{TiO}_2$  photocatalytic activity differ significantly. For example, X-type zeolite has a higher static adsorption capacity for  $\text{CO}_2$  gas than A-type zeolite, X-type zeolite is more suitable as a photocatalyst carrier because its ion exchange capacity is greater than that of Y-type zeolite. Different types of zeolite molecular sieve-supported  $\text{TiO}_2$  exhibit higher photocatalytic activity when compared to pure  $\text{TiO}_2$  powder. Wang J J et al. also reached the same conclusion as mentioned above (Wang et al., 2015).

## BIOGENIC SEDIMENTARY ROCK DIATOMITE LOADED WITH $\text{TiO}_2$

Diatomite with consists of amorphous silica ( $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ ) essentially derived from the skeletons of ancient diatoms. It is a biogenic siliceous sedimentary rock with a large surface area, high porosity, high permeability, small particle size, low density, thermal resistance, and chemical stability. Their surface contains numerous (Si-OH) silanol groups, which can form hydrogen bonds with a variety of contaminants. Diatomite could serve as an effective support material for nano titanium dioxide particles. **Figure 6** shows a schematic diagram of the surface structure of diatomite (Cherrak et al., 2020).

Zhang G et al. used hydrolysis and deposition to create a  $\text{TiO}_2$ /diatomite composite photocatalyst. The  $\text{TiO}_2$ /diatomite composite material demonstrated higher photocatalytic activity than pure  $\text{TiO}_2$ , demonstrating that Nano  $\text{TiO}_2$  particles have stronger formaldehyde adsorption capacity and good dispersibility after the addition of diatomite (Zhang et al., 2017). Zhang J prepared a  $\text{TiO}_2$ /diatomite photocatalyst by hydrolytic deposition method using titanium tetrachloride as a precursor. It has been demonstrated that adding a small amount of sulfate ion promotes the formation of the anatase phase and inhibits the transformation from anatase to rutile (Gao and Zhang 2001; Zhang et al., 2016). At the same time, the sulfate ions immobilized on the surface of  $\text{TiO}_2$ /diatomite have a strong affinity for electrons, capturing the photogenerated electrons, preventing electron-holes recombination (Zhang et al., 2016).

## CARBON-CONTAINING MINERAL BLACK TALC LOADED WITH $\text{TiO}_2$

As a kind of layered silicate mineral, black talc is widely used. Compared with other silicate minerals, black talc has good surface

affinity, chemical stability, and thermal stability. Meanwhile, there is a carbon layer between the black talc layers and before the talc crystal grains that has a high capacity for organic pollutant adsorption. It can adsorb organic pollutants around the black talc, increasing the concentration of pollutants near the minerals and thus increasing the photocatalyst's catalytic efficiency. The author prepares a titanium dioxide/black talc composite photocatalyst using black talc as a carrier, implements the indirect light degradation method, and completely exploits the adsorption-degradation coupling of black talc, which greatly reduces the time of light. **Figure 7** shows schematic diagram of photocatalytic performance enhancement mechanism of  $\text{TiO}_2$ /Black Talc composite material (Shuai et al., 2021).

## CONCLUSION AND OUTLOOK

Nano- $\text{TiO}_2$  composite catalyst supported by nonmetallic minerals combines the adsorption and capture function of mineral materials with the photocatalytic degradation function of nano- $\text{TiO}_2$ , which not only addresses the issues that pure nano- $\text{TiO}_2$  is difficult to use and recycle but also improves the photocatalytic performance of nano- $\text{TiO}_2$  materials and promotes the practical application of nano- $\text{TiO}_2$  materials. In addition, the composite material also opens up a new way for the efficient utilization of silicate nonmetallic minerals. Nano- $\text{TiO}_2$  composite catalysts supported by nonmetallic minerals are expected to have a successful potential application.

However, the current mineral material loaded  $\text{TiO}_2$  photocatalyst still has challenges to be solved:

- 1) The photocatalyst is still in the laboratory stage and is often treated for a single pollutant, which makes it difficult for materials to deal with pollutants in complex systems. Therefore, it is necessary to further build a mineral adsorption degradation synergistic catalytic system to prepare porous mineral supported composite catalytic materials with better performance.
- 2) There is still a certain gap between laboratory preparation and industrial production, and it is necessary to solve the problems of technology, equipment and production efficiency in the industrial production process.
- 3) The conversion efficiency of photocatalytic materials to visible light is relatively low, and the mechanism of action on mineral carriers is not clear enough. It is necessary to borrow more advanced analysis and testing methods to study its compounding principle and improve the utilization rate of light.

## AUTHOR CONTRIBUTIONS

XY: conceptualization, methodology, data curation, and writing - original draft preparation. JW: conceptualization, investigation, methodology, and funding acquisition. FR and GD: conceptualization, writing - review and editing, supervision. HS: conceptualization, investigation, and methodology. All authors contributed to the article and approved the submitted version.



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