

[BMIM]BF₄-Chlorophyll sensitized Nano-TiO₂ Photocatalytic Degradation of Methyl Orange

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August, 2020

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Abstract

Nowadays, leather products have popularity globally. However, the waste water produced in the dyeing process has always been problems in industrial production. Recently, considerable attention has been paid to photocatalytic degradation. In this project, we changed the structure and absorption wavelength range of TiO₂ to degrade methyl orange, a representative of pollutants during dyeing process. By utilizing the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF₄), the specific surface area of TiO₂ was enlarged, and the particle size of TiO₂ was decreased by the function of ionic liquid(IL), thereby the photocatalytic degradation efficiency was improved. Additionally, to extend the absorption wavelength range of the IL-TiO₂ catalyst to the visible region, the catalyst was sensitized by chlorophyll through physical adsorption. The degradation efficiency was characterized by the UV-visible spectrophotometer, which reaches 79.8% under visible light. The influence of the ratio of [BMIM]BF₄ and tetrabutyl titanate, and the chlorophyll concentration on the degradation efficiency were also investigated. It was concluded that the optimum preparation condition of catalyst for degrading under visible light was: the ratio of [BMIM]BF₄ and tetrabutyl titanate was 3:13, the concentration of chlorophyll was 40 ppm; pH of tetrabutyl titanate mixing solution was 6, and calcination temperature of IL-TiO₂ was 180 °C; sensitization temperature was 25 °C and sensitization time is 24 h.

Keywords: Photocatalytic, Chlorophyll Sensitization, TiO₂, Methyl Orange

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1.Introduction

1.1 Present Situation of Dyeing waste water Treatments

Dyeing waste water is harmful to human health. Some heavy metal ions discharged into the water will contaminate the ecosystem and also affect human health. The main characteristics of dyeing waste water are high chromatic, high toxicity, and complex organic components. These characteristics make it difficult to degrade. Currently, the acceptable waste water treatment methods mainly include physical, chemical, and biological methods.

Adsorption is mainly used in the physical methods. The adsorption method uses porous solids to accumulate or condense one or more components in a fluid mixture on the surface to achieve the purpose of separation.^[1] Li *et al.*^[2] proved that active carbon has the most superior performances in Chemical Oxygen Demand removal, Dissolved Organic Carbon removal, and adsorption capacity characterization. Vimonses *et al.*^[3] indicated that sodium bentonite had the best adsorption performance. Qiu *et al.*^[4] proved that factories could use activated attapulgite has a high degradation rate for cationic dyeing waste water as a pre-treatment method. However, there are lots of challenges on after-treatments in the adsorption method, and it is expensive due to the considerable usage of absorbent materials.

The chemical method mainly includes coagulation, electrolysis, photocatalytic redox, and so forth. Coagulation is the most common, efficient, and economical method in the industry. By adding the flocculant to the azo dye waste water, the colloids and suspended solids in the water under the action of the flocculant form flocs precipitation through instability, mutual collision and agglomeration transfer, and the particles are separated from it, thereby treating waste water.^[5] The

internal electrolysis method degrades the contaminants through the reduction of iron and hydrogen and the action of electric field. The essence is the combination of electrochemistry and redox. Although the internal electrolysis method can effectively remove the harmful substances in the dye waste water, there are still some problems that need to be improved. For example, the particle size of iron filings are small and will disappear during the process, which reduces the degradation efficiency.^[6]

The biological method is mainly to purify wastewater by using microorganisms to adsorb and decompose contaminants. The microorganisms usually work in an aerobic environment, and the organic matter in the dyeing wastewater could be converted into inorganic matters. Li *et al.*^[7] illustrated that the composite bacterial activated sludge composed of two high-efficiency degrading bacteria has a stronger ability to treat disperse dye waste water than that of a single strain. However, the disadvantage of the biological method is that it requires high water quality and high operating costs.

In conclusion, these wastewater treatment methods have their pros and cons. Photocatalytic treatment methods has attracted much attention within global; many types of researches focused on it. The purpose of our study is to prepare [BMIM]BF₄-Chlorophyll sensitized TiO₂ catalyst to improve the ability to degrade waste water under visible light.

1.2 Properties of Nano-TiO₂

1.2.1 Crystal structure

There are three essential forms of TiO₂: rutile, anatase, and brookite. Rutile type is the most stable structure, which will not transform and decompose under high temperatures. Both rutile and

anatase-TiO₂ belong to the square system, but only anatase-TiO₂ is the best photo catalyst. Brookite-TiO₂, belongs to the orthorhombic system, is the most unstable type. Brookite and anatase are likely to transform to rutile-TiO₂ at high temperatures.^[8-10] The reason why photocatalytic properties of anatase are higher than that of rutile is rutile has a smaller bandgap (E_g of anatase-TiO₂ is 3.3eV, E_g of rutile-TiO₂ is 3.1eV), and its more positive conduction band blocks the decrease reaction of oxygen. Additionally, anatase-TiO₂ crystal lattice holds extra defects and dislocations, causing extra oxygen positions to arrest electrons. However, rutile-TiO₂ is the most stable form of crystal structures with the best crystalline state.

1.2.2 Photocatalytic

When the TiO₂ electrode of the chemical cell is irradiated by the light with a wavelength of less than 415 nm, hydrogen forms at the black platinum electrode at the other end. Scientists have proved that nano-TiO₂ has the superb photocatalytic ability and has practical application in many fields such as environmental pollution treatment and gas purification.

The photocatalytic mechanism of nano-TiO₂ is: as an N-type semiconductor, there is a forbidden band between the valence band full of electrons and the empty conduction band. When the energy of irradiated light is greater than the width of forbidden band, the electrons in the valence band captivate energy and jump to the conduction band are converted into free electrons with potent reduction property. Simultaneously, an intense oxidizing property hole forms in the valence band. The free electrons diffuse to surface of particle and have a redox reaction with the material adsorbed on the surface of the particle. The hole could react with water and hydroxide to form high active carboxyl, which could mineralize the organic matter without selection. The free electrons in the conduction band could form oxygen ion with intense oxidizing property, and the oxygen ion could

degrade the pollutant.

Nano-TiO₂ has a remarkable shielding effect showing by its ability to absorb and scatter ultraviolet rays. As an N-type wide forbidden band semiconductor, nano-TiO₂ can absorb ultraviolet light with energy higher than the forbidden band. Also, nano-TiO₂ is a high refractive index material, which can scatter the longwave ultraviolet rays well. One practical application is that adding nano-TiO₂ with fabulous UV shielding ability into a leather finishing agent can improve the anti-ultraviolet aging ability of the coating. [11] Figure 1 reveals the process of TiO₂ photocatalysis.

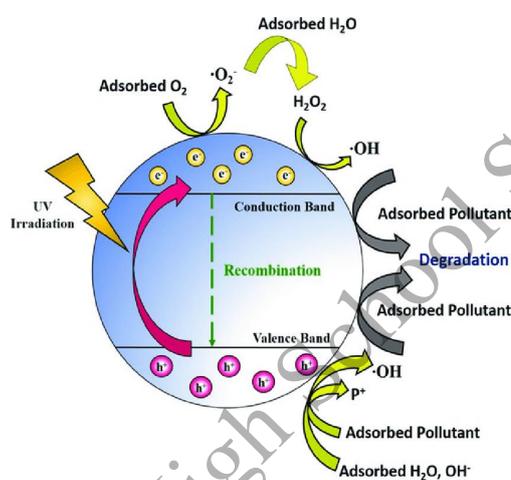


Fig.1. Process of TiO₂ Photocatalysis^[12]

Table 1 Equations of Photocatalytic Process

Equations
$\text{TiO}_2 + h\nu \longrightarrow e^- + h^+$
$h^+ + \text{OH}^- \longrightarrow \cdot\text{OH}$
$h^+ + \text{H}_2\text{O} \longrightarrow \cdot\text{OH} + \text{H}^+$
$e^- + \text{O}_2 \longrightarrow \cdot\text{O}_2^-$

1.3 Ionic Liquid Template

IL is a type of salt, and it is a liquid at room temperature and normally made up of organic cations and inorganic anions. Matched with traditional organic solvents and electrolytes, ionic liquids have many advantages. It has nonvolatile properties and can be used as an environmentally friendly solvent to reduce environmental problems caused by volatilization. It has a wide range of stable temperature and can separate readily from other substances.^[13]

According to the different organic cations, we can divide IL into four categories^[14]: Imidazoles, Pyridines, Quaternary ammoniums, Quaternary phosphoniums. The low surface of the ionic liquid can prompt the inside substances to be stable, improving the nucleation efficiency of inorganic materials, and have a smaller particle size.^[13] Wang et al.^[15] disclosed that the ionic liquid [BMIM]BF₄ has a significant effect on the formation of the final shape of ZnO: in the presence of a small amount of ionic liquid.

In our study, [BMIM]BF₄ is used for changing the crystal structure of TiO₂. [BMIM]BF₄ is a kind of template with a specific structural orientation, prompting TiO₂ to form orderly. Extended hydrogen bonds are produced in the liquid state, forming a better structure system driven by entropy to make TiO₂ spontaneously form an ordered structure and increase the content of surface hydroxyl.

1.4 Chlorophyll Sensitization

TiO₂ has a wide bandgap which is about 3.2eV and can only absorb ultraviolet light; the response range can extend through surface sensitization, and thus the light utilization rate can be improved. As long as the photosensitizer's excited state is more conductive than the semiconductor, the potential enables the electrons generated by visible light excitation to be transported from the

photosensitizer to the conduction band of the semiconductor, effectively extending the excitation wavelength of the TiO₂ photo catalyst to the visible light range. The sensitization methods include dipping compound sensitization method(CdS/TiO₂), organic sensitization, inorganic sensitization, and electricpolymer sensitization. Chlorophyll Sensitization is a type of organic sensitization.^[16] It is mainly uses for solar cells, and there is relatively little research on the degradation of waste water. Chlorophyll is a green pigment that exists in the leaves and stems of plants, and it is a colored hetero-cyclic compound of porphyrins. Figure 2 reveals the structure of chlorophyll derivative. Furthermore, it is a crucial part of photosynthesis in plants, which plays a role in absorbing and converting light energy in plants. The role of chlorophyll molecules is to reduce light-generated electricity by reacting with light-generated holes. The recombination rate of electrons and holes promotes the yield and transfer efficiency of TiO₂ photo-generated electrons; the excited state chlorophyll molecules in which the photon energy is absorbed, and thus it is easier to react with the holes (h⁺) in TiO₂. It reduces the loading rate of photogenerated electrons and holes more effectively.^[18] However, the sensitization effect of directly extracting chlorophyll from natural plants is not satisfied. Because it physically adsorbs with TiO₂, the absorbed photons cannot enter the conduction band of TiO₂.^[19] Consequently, the target of our study changes to copper sodium chlorophyll, which has similar properties.

the crystal structure, and nitrogen adsorption-desorption analysis was used to analyze its surface area, pore size and pore volume. The research successfully design [BMIM]BF₄-Chlorophyll sensitized TiO₂ catalyst and provides a practical reference for the treatment of dyeing waste water.

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2. Experiment Section

2.1 Materials

Table 2 Experiment Reagents

Material	Purity	Manufacturer
Tetrabutyl Titanate	Chemical Pure	Sinopharm Chemical Reagent Co., Ltd
Hydrochloric Acid	Analytical Reagent	Beijing Chemical Works
[BMIM]BF ₄	Analytical Reagent	Shanghai ChengJie Chemical Co.,Ltd
Copper Sodium Chlorophyll	Analytical Reagent	Shanghai Macklin Biochemical Co.,Ltd
Methyl Orange	Analytical Reagent	Sinopharm Chemical Reagent Co., Ltd
Deionized Water	Made by laboratory	

Table 3 Main Experimental Apparatus

Apparatus	Type	Manufacturer
Analytical Balance	ME204E/02	METTLER TOLEDO
Magnetic Stirrer	ZNCL-BS	Aibote Henan Science&Technology Development Co.,Ltd
Vacuum Drying Oven	DZF-6050	Shanghai Yiheng Scientific Instrument Co., Ltd.
Muffle Furnace	SX-G07103	Tianjin Zhonghuan Furnace Corp.
Grow Lights	C21GL-CE27	Shanghai Sansi Electronic Engineering Co.,Ltd.
X-ray Diffractometer	Empyrean	PANalytical B.V.,Holland
UV-VIS Spectrophotometer	UV2550	Shimadzu Corp.
Surface Area & Porosity Analyzer	ASAP 2460	Micromeritics Instrument Co., Ltd.

2.2 Catalyst Preparation

2.2.1 [BMIM]BF₄-TiO₂ Catalyst

Ionic liquid [BMIM]BF₄, which ratio of it to tetrabutyl titanate are 3:13 or 6:13, were dissolved in 65 ml deionized water, and pH of the solution was adjusted to 6 with hydrochloric acid. 6.5 ml of tetrabutyl titanate was added to the mixed solution; after stirring vigorously for 30 min. The final result was moved to the Teflon-lined stainless steel autoclave lined for hydrothermal reaction. The sample reacted at 180 °C for 10 h and cooled to room temperature. The white precipitate obtained was rinse three times with ethanol, twice with deionized water, and then dried under vacuum at 80 °C for 10 h in vacuum. Commercial TiO₂ was used as control check, denoting as TiO₂. IL-TiO₂ are denoted as A₁ (ratio is 3:13) and A₂ (ratio is 6:13).

2.2.2 Chlorophyll-Sensitization

10 mg of copper sodium chlorophyll was put into 100 ml of deionized water to make 100 ppm solution, then the solution was diluted into 20 ppm, 30 ppm, and 40 ppm; after that process, sealed and mixed samples evenly. Then 0.2 g of A₁ was added, and stirred for 24 h at 20 °C in darkness. The prepared mixture was dried at 120 °C in a vacuum oven in darkness for 11 h. The obtained samples were denoted as A₁B₁ (20 ppm), A₁B₂ (30 ppm), A₁B₃ (40 ppm) respectively. Figure 3 shows the process of preparing IL-Chlorophyll-TiO₂ catalyst straightforwardly.

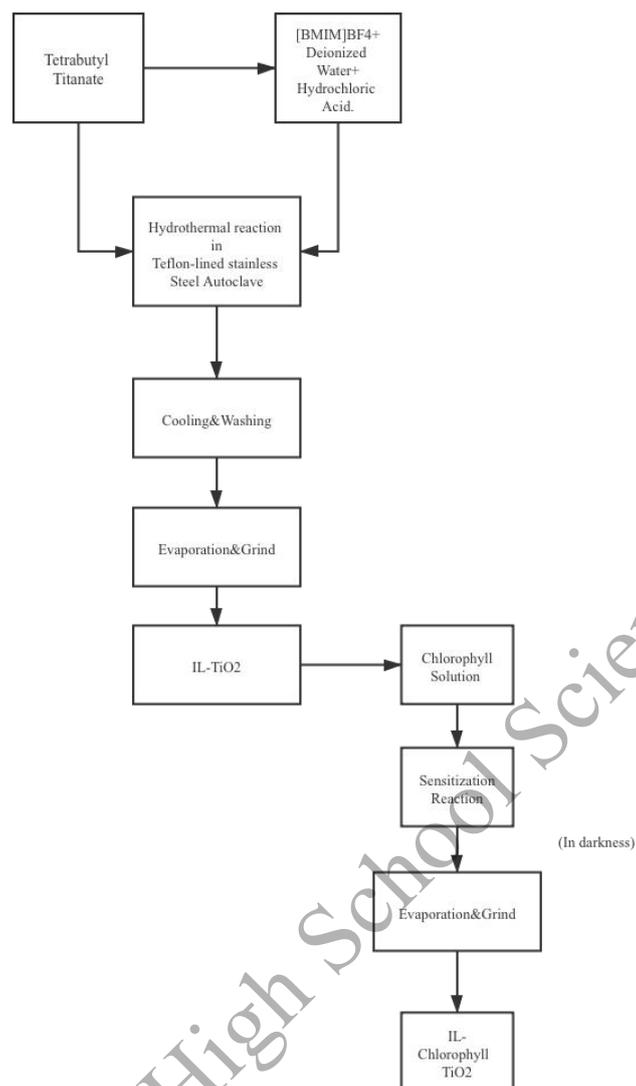


Fig.3. The flow chart of preparing IL-Chlorophyll-TiO₂ catalyst

2.3 Experiment Process

2.3.1 Standard Curve

The experiment utilized methyl orange as the degradant to evaluate the photocatalysis result of this synthesized catalyst. 8 mg methyl orange were weighed by analytical balance and displaced into 100 ml volumetric flask; then the solution was diluted to 20 ppm, 40 ppm, 60 ppm and 80 ppm. UV-VIS spectrophotometer and 3 cm cuvette were used, and the absorbance A were measured at

450 nm with blank reagent as a reference for baseline correction.

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Table 4 Data of Standard Curve

Concentration (ppm)	20	40	60	80
Absorbance A	0.762	1.383	1.977	2.684

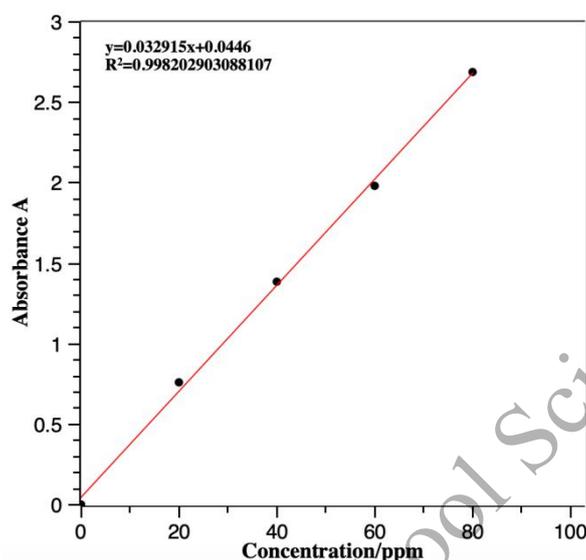


Fig.4. Standard Curve of Methyl Orange

Figure 4 illustrates the standard curve's equation of concentration-absorbance is $y=0.032915x+0.0446$. $R^2=0.998603176107942$ (y represents absorbance, x represents concentration)

2.3.2 Experiment Method

The photocatalytic result of the catalyst was investigated by degrading methyl orange solution under ultraviolet/visible light irradiation. 5 ml methyl orange (47 ppm) solution was used and 5 mg $\text{TiO}_2/\text{IL-TiO}_2/\text{IL-chlorophyll-TiO}_2$ catalyst was added in a watch glass. Before irradiation, the solution was placed in the dark for 30 minutes to achieve adsorption-desorption equilibrium. Samples were placed under ultraviolet light or using 24 W C21GL-CE27 grow lights as visible light condition. The catalyst's photodegradation rate was observed by spotting the svariation in

absorbance at 450 nm between defined time intervals using the UV - Vis spectrophotometer. Then, absorbance was substituted into the equation obtained from the standard curve to calculate the concentration of methyl orange after degradation in each time period. Eventually, the degradation rate using a formula was calculated:

$$\text{Degradation rate} = \frac{C_0 - C_t}{C_0} \times 100\% \text{ (} C_0 \text{ represents initial concentration, } C_t \text{ represents concentration}$$

after time t 's degradation)

2.4 Characterization Analysis

2.4.1 XRD Analysis

XRD Analysis can be used to analysis the crystal structure of $\text{TiO}_2/\text{IL-TiO}_2/\text{IL-chlorophyll-TiO}_2$ catalyst because each substance has particular crystal structure. This study uses Empyrean equipped with $\text{Cu } \alpha$ radiation at 200 mA and 40 kV. The scan range 2θ is 10° - 90° , and step width is 0.01 degree. Scherrer formula can be used to determine average cyrstallite size to compare catalysts.

2.4.2 FT-IR Analysis

FT-IR Analysis extensively applies into organic compounds to analyze their properties and structures. $\text{TiO}_2/\text{IL-TiO}_2/\text{IL-chlorophyll-TiO}_2$ catalysts were mixed with KBr in a certain proportion, then fully grind and press the sample. This study utilizes Nicolet 380 to analyze the structure of catalysts.

2.4.3 Nitrogen Adsorption-Desorption Analysis

Nitrogen adsorption-desorption analysis is a method to determine the specific surface area and pore structure of catalysts. The N₂ adsorption-desorption method is conducted under liquid nitrogen conditions, and the adsorption-desorption isotherm is obtained. This study uses ASAP 2460 for analysis, using N₂ at 77.35 K. All the samples were outgassed in vacuum at 120 °C for 4 h.

BET equation and BJH model were used to obtain surface area, pore volume and pore size by obtaining from desorption and adsorption curves.

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3. Experiment Results

3.1 Experiment Data

Table 5 Experiment data (UV Light)

Sample	Ratio of IL to tetrabutyl titanate A (ml)	Chlorophyll Concentration B (mg/L)	Final Degradation rate (%)
TiO ₂	0	0	71.56
A ₁	3:13	0	88.43
A ₂	6:13	0	86.93
Best sample for degrading		A ₁	

Table 6 Experiment data (Visible Light)

Sample	Ratio of IL to tetrabutyl titanate A(ml)	Chlorophyll Concentration B(mg/L)	Final Degradation rate (%)
TiO ₂	0	0	0
A ₁	3:13	0	0
A ₂	6:13	0	0
A ₁ B ₁	3:13	20	58.58
A ₁ B ₂	3:13	30	59.95
A ₁ B ₃	3:13	40	79.80

Table 7 Photocatalytic Performance Comparison of different Catalysts under Visible Light

Type of catalyst	Quantity of catalyst (mg)	Quantity of solution (ml)	Degradation Rate (%)	Time (h)
TiO ₂	5	5	0	3
Bi - doped TiO ₂ [23]	18	5	35	3
RGO /TiO ₂ [21]	5	5	50	3
Ti-Cr-MCM-48 [22]	10	5	70	3
A ₁ B ₃	5	5	79.8	3

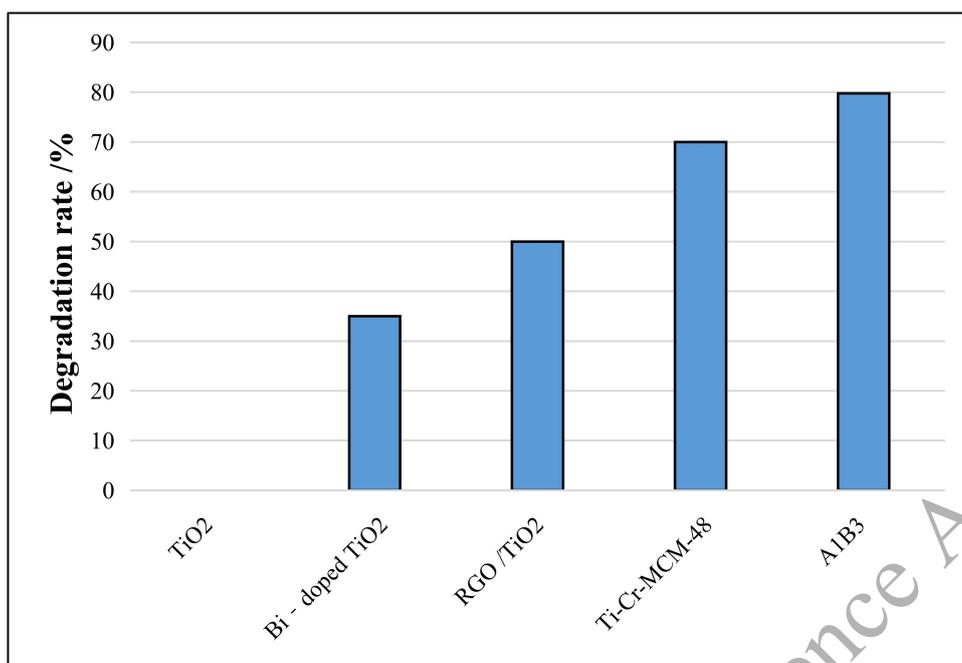


Fig.5. Photocatalytic Performance Comparison of different Catalysts under Visible Light

Table 5 and 6 show the degradation data of different groups explicitly. Table 7 and Figure 5 reveal the performance comparison explicitly. First, it is shown that the commercial TiO₂ does not have photocatalytic performance in visible light condition. A₁B₃ has the best performance of all catalysts which approach 79.8%. It uses relatively less quantity of catalyst than Ti-Cr-MCM-48 and Bi - doped TiO₂, indicating better performance with less amount. Consequently, [BMIM]BF₄-chlorophyll sensitized TiO₂ catalyst has noticeable performance in photocatalysis with comparison of other synthesized catalyst.

3.2 Characterization Analysis Results

3.2.1 XRD Analysis

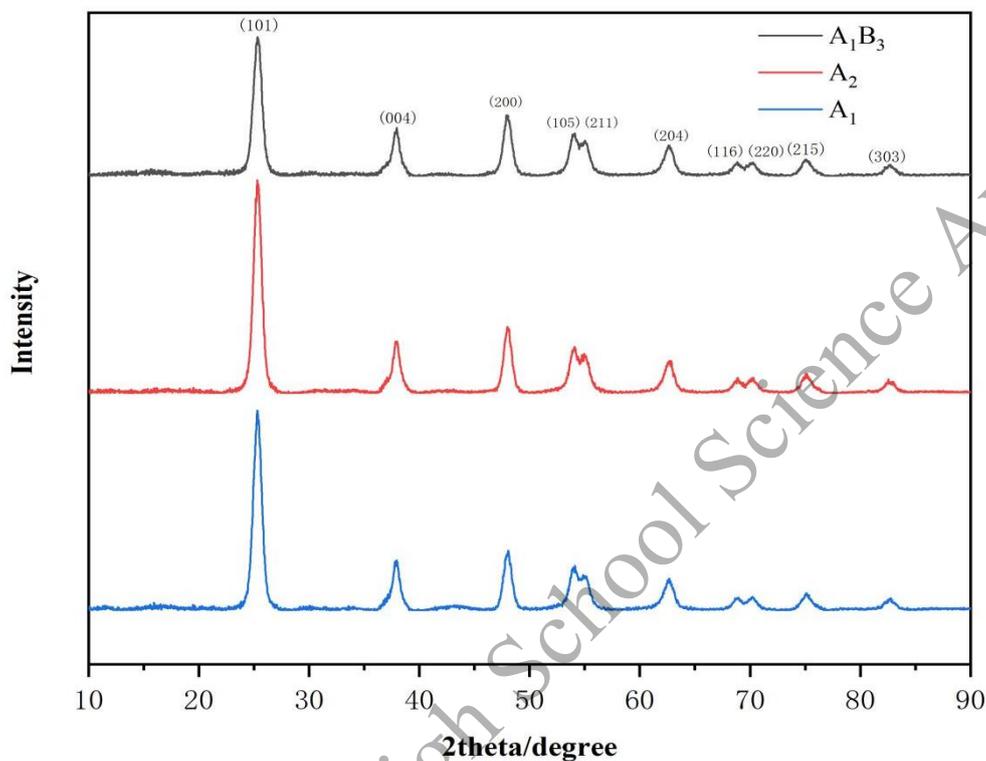


Fig.6. XRD Patterns of TiO₂/IL-TiO₂/IL-chlorophyll-TiO₂ catalyst

Figure 6 shows the wide-angle XRD patterns of samples A₁, A₂, and A₁B₃ prepared by the ionic liquid assisted method. It can be seen from Figure 6 that the peaks of 2θ value at 25.3°, 36.9°, 37.8°, 48.0°, 53.9°, 55.1°, 62.7°, 68.8°, 70.3°, 75.0°, 82.1° and 82.7° correspond to crystal planes of anatase (101), (103), (004), (200), (105), (211), (204), (116), (220), (215), (303) and (224). The positions and relative intensities of the diffraction peaks of three sample are consistent with those of the standard card (JCPDS 89-4921). The position of diffraction peaks at 53.9° and 55.1° indicates the formation of anatase, reducing the formation of brookite. This XRD analysis reveals that the addition of IL and chlorophyll will not change the crystal structure of TiO₂.

The crystallite sizes of each sample can be obtained from Scherrer's formula. The crystallite sizes

are shown in Table 8. The crystallite sizes of each sample are significantly reduced because the ionic liquid was added, promoting the crystallization of anatase and retarding the nucleation time to increase the nucleation rate. Crystallite sizes of A₁ and A₂ are significantly less than commercial TiO₂ because of the function of IL. However, according to the physical adsorption of chlorophyll, the crystallite size of A₁B₃ is a trifle more significant than that of A₁ and A₂, but still less than commercial TiO₂. The shorter crystallite size is, the better photocatalytic ability it has: so the additions of ionic liquid and chlorophyll can improve the photocatalytic ability, and chlorophyll can also expand the absorption range into visible light by using XRD Analysis and Scherrer's formula.

Table 8 Crystallite size of TiO₂/IL-TiO₂/IL-chlorophyll-TiO₂ catalyst

Sample	TiO ₂	A ₁	A ₂	A ₁ B ₃
Crystallite Size (nm)	16.3	9.7	10.5	11.1

3.2.2 FT-IR Analysis

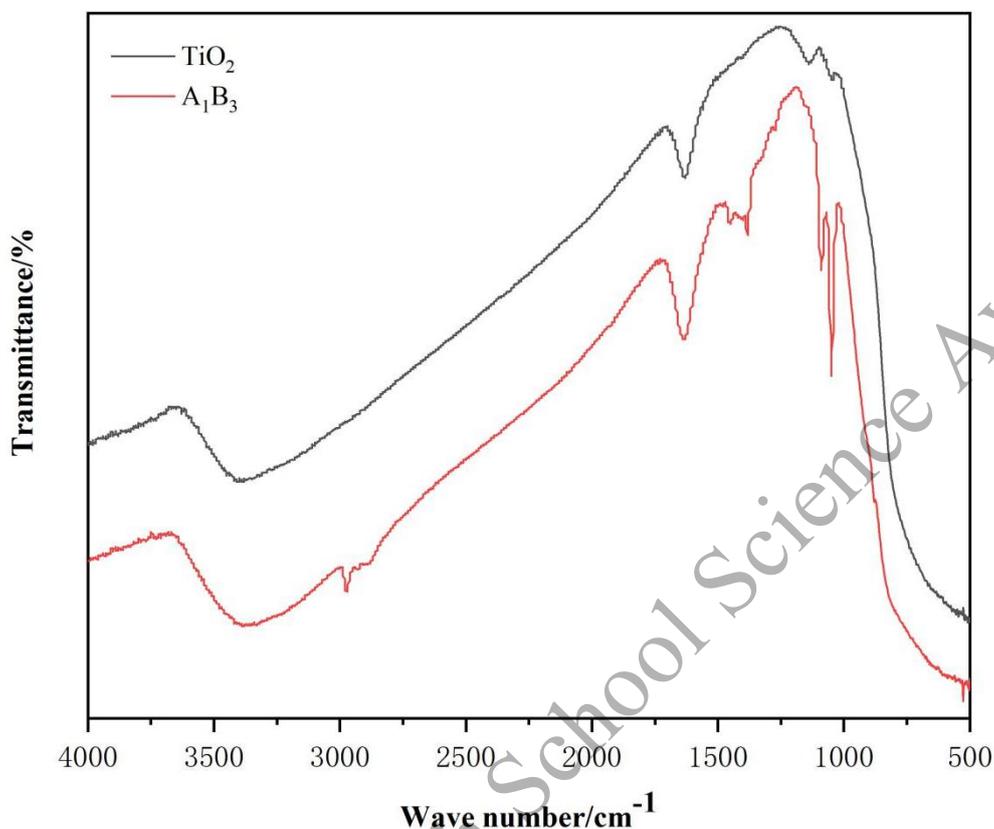


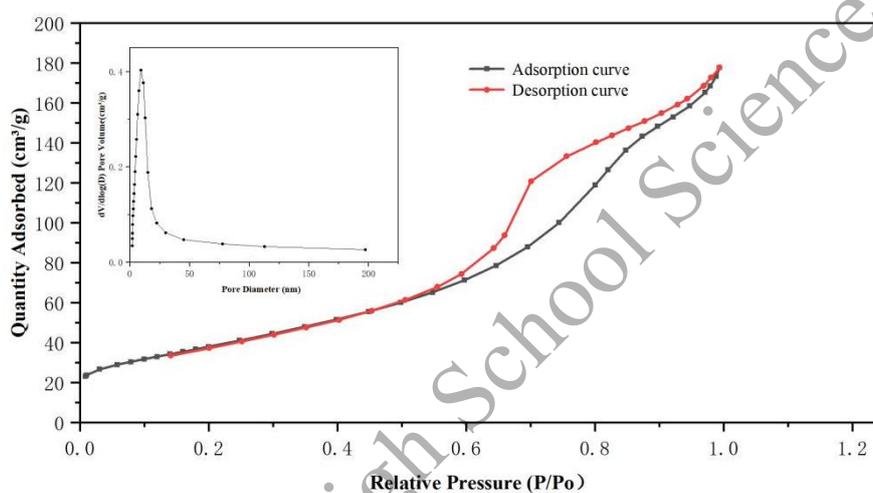
Fig.7. The FT-IR Spectra of TiO₂/IL-chlorophyll-TiO₂ catalyst

As shown in Figure 6, after the treatment of the IL-chlorophyll-TiO₂/TiO₂ catalyst, several peaks appeared in the spectrum. Peaks at 3385 cm⁻¹ could be ascribed to the stretching vibration of O-H. The peaks at 1629 cm⁻¹ could be allocated to the bending vibration of O-H. Peaks at 526 cm⁻¹ are the Ti-O-Ti characteristic peak. According to this analysis, the prepared catalyst has the characteristics of functional groups of TiO₂. The asymmetric stretching vibration peak of saturated C-H is at 2972 cm⁻¹ peaks, which is a characteristic of the imidazole ring, indicating the existence of methyl in [BMIM]BF₄. Besides, the peak at 1060 cm⁻¹ can be ascribed to B-F vibration in BF₄⁻.

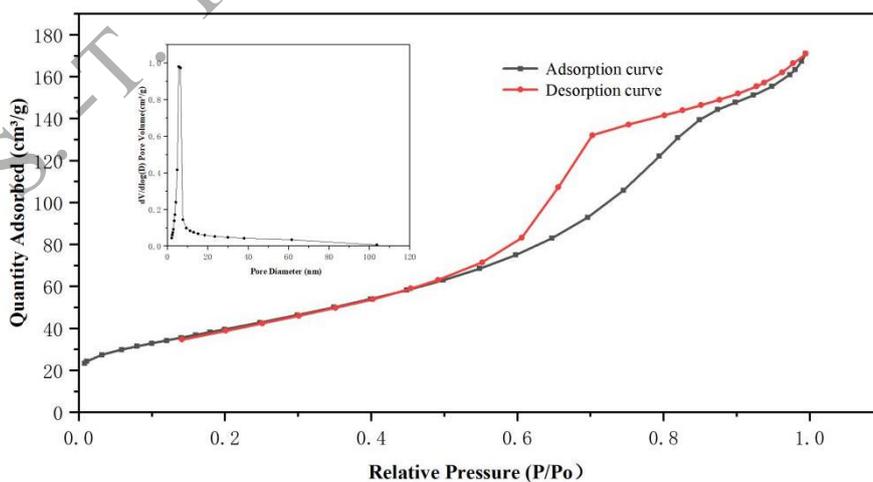
The peak at 1383 cm⁻¹ can be described as bending vibration of —CH₃— in copper sodium chlorophyll functional group. In-plane bending vibrations of C=N, C-C, C-N, are located at 1050

cm⁻¹.^[24] According to this analysis, the prepared catalyst also has characteristics of functional groups of copper sodium chlorophyll, so chlorophyll was successfully added in the IL-TiO₂ sample. In conclusion, copper sodium chlorophyll and [BMIM]BF₄ is adsorbed physically on TiO₂ and thus changed its functional group and structure.

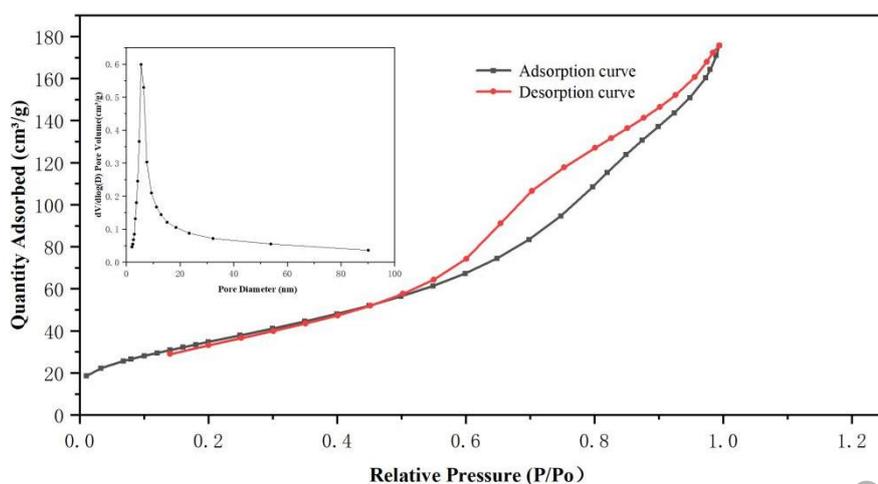
3.2.3 Nitrogen Adsorption-Desorption Analysis



(a) A₁



(b) A₂



(c) A₁B₃

Fig.8. Nitrogen Adsorption-Desorption Isotherms of IL-TiO₂/IL-chlorophyll-TiO₂ catalysts and pore distributions of those catalysts by BJH model

According to Figure 8, the isotherms of samples A₁, A₂, and A₁B₃ are typical V type isotherms, and the H2 type hysteresis regression line unique to mesoporous materials appears at the medium pressure ends. It can be seen that the samples are mesoporous materials. At the ends of high pressure, the adsorption capacity of the samples did not increase significantly, indicating that the sample particles accumulated small pores. According to the pore distribution by BJH model, it demonstrates that the pore sizes of three samples are about 10nm because their percentages at 10 nm are highest of three figures, showing the mesoporous structures.

It can be seen from Table 9 by using BET equation, obtaining from relative pressure from 0.05 to 0.35, that the specific surface area of A₁ is larger than that of A₂, and the pore diameter and pore volume are smaller than A₂. This could be attributed to the existence of more ionic liquids in A₂, causing the nucleation rate rapid and weakening the ability to use as a template and guide the structure. The specific surface area of A₁B₃ may be relatively low due to the physical adsorption of chlorophyll on the surface of samples; however, both of them have higher specific surface area,

smaller pore volume and pore size than commercial TiO₂, indicating better photocatalytic properties.

Table 9 BET surface area, Pore volume and Pore size of TiO₂/IL-TiO₂/IL-chlorophyll-TiO₂ catalyst

Sample	TiO ₂	A ₁	A ₂	A ₁ B ₃
BET Surface Area(m ² /g)	61.66	145.821	139.702	130.931
Pore Volume(cm ³ /g)	0.262	0.265	0.280	0.271
Pore Size(nm)	15.00	6.015	6.785	6.748

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3.3 Influence of Different Variables on Degradation Rate

3.3.1 Influence of Ratio of [BMIM]BF₄ to Tetrabutyl Titanate on Degradation Rate

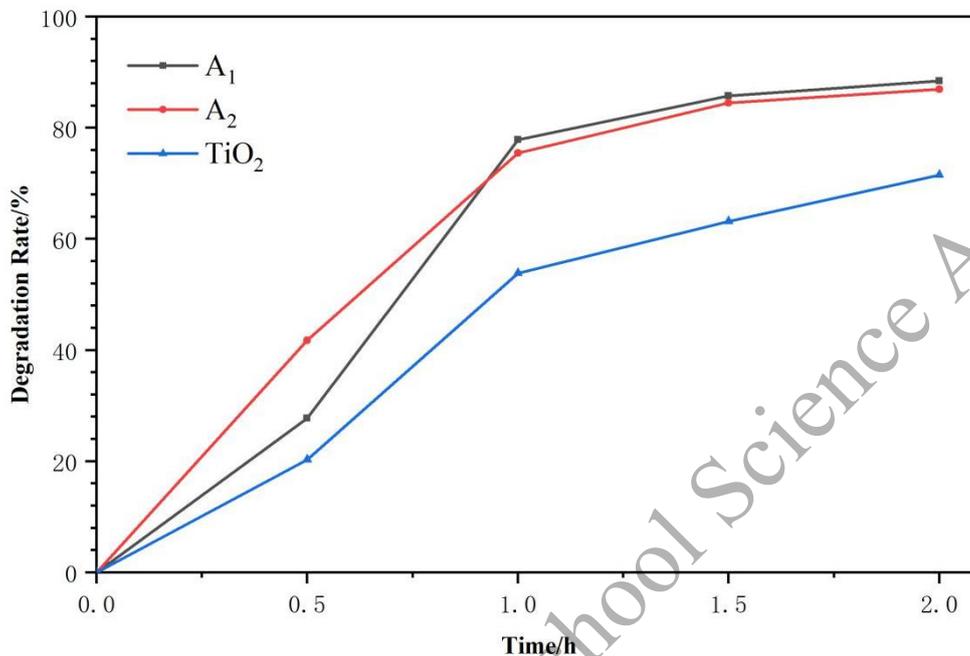
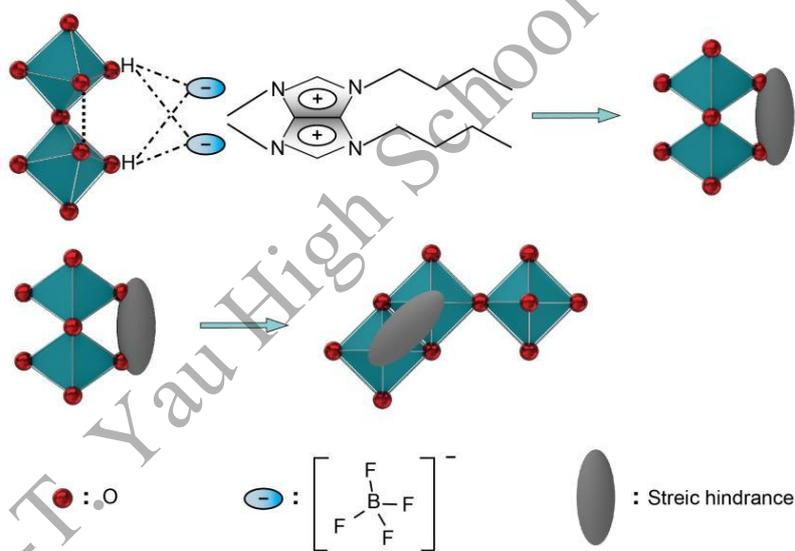


Fig.9. Line chart of Methyl Orange Degradation Rate to Time (UV Light condition)

It can be seen from Figure 9 that both commercial TiO₂ and IL-TiO₂ can degrade methyl orange under ultraviolet light. However, under the same experimental conditions, the degradation rate of the A₁ group approached 88.43% at 2 h, which was higher than the other two groups. According to several characteristic analysis above, the crystallite size of A₁ (approximately 9.7 nm) is smallest of three; also, its specific surface area is larger than others. [BMIM]BF₄ retards the nucleation process of TiO₂, increasing the nucleation rate and forming crystals with small particle diameters. However, though there are larger ratio of [BMIM]BF₄ to tetrabutyl titanate in A₂, the degradation rate of it is lower than A₁. It can be speculated that with greater ratio, the crystal nucleus grows fastly, resulting in the increase of the particle size, and decrease of the specific surface area; those two characteristics can be revealed in Table 8 and 9 above. Although the crystal structure is anatase type

which has better photocatalytic activity, it cannot degrade methyl orange under same conditions because it cannot absorb visible light according to the UV–Visible Diffuse Reflectance Spectroscopy. Mechanisms shown in Figure 10 demonstrate the function of ionic liquid in the synthesizing process, BF_4^- forms hydrogen bonds with TiO_6 octahedrons and $[\text{BMIM}]^+$ combine with each other by $\pi-\pi$ bond; then, $[\text{BMIM}]^+$ and BF_4^- closely arrange by the coulomb force. Under the synergistic effect of hydrogen bond, $\pi-\pi$ bond, and coulomb force, the TiO_6 octahedrons tend to be coedge bonded between the fixed edges. The fixed sites of the TiO_6 octahedrons are occupied by the larger ionic liquid, forming steric hindrance.



•Fig.10. The Schematic Diagram of the formation of IL-TiO₂

3.3.2 Influence of Chlorophyll Concentration on Degradation Rate

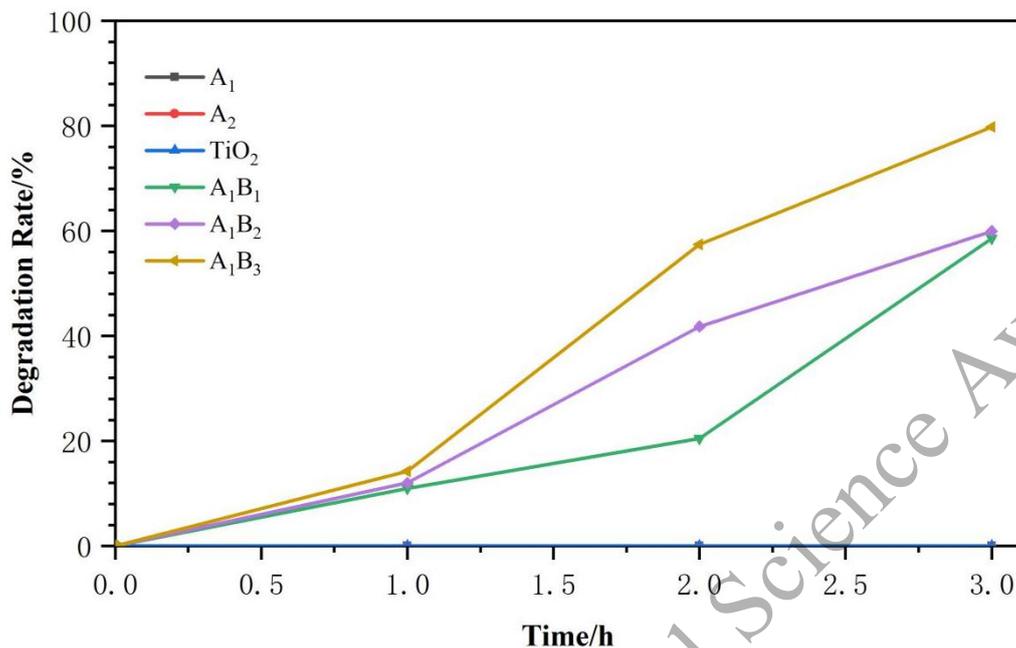


Fig.11. Line chart of Methyl Orange Degradation Rate to Time (Visible Light condition)

It can be seen from Figure 11 that both commercial TiO₂, A₁ and A₂ cannot degrade methyl orange under visible light. However, under the same experimental conditions, groups which adding chlorophyll can degrade methyl orange. Of all three, A₁B₃ has the best optimum photocatalytic efficiency of 79.80%. As the amount of chlorophyll adsorbed increases, its absorption ability of visible light also increases. Although a small amount methyl orange can be decomposed by chlorophyll itself, its degradation rate increased. Under the function of ionic liquid, the specific surface area is increased and the particle size is reduced. After the absorption of chlorophyll, the absorption wavelength range of catalyst is shifted from 200-400 nm to 200-600 nm, so that the catalyst responds to visible light. of adsorption on IL-TiO₂ can increase its degradation rate. In addition, the rough surface of the catalyst can generate diffuse reflection, increasing efficiency of absorbing light. It may be assumed that with the irradiation of visible light, the chlorophyll molecules adsorbed on the surface are excited to emit electrons, and the electrons are transferred to

IL-TiO₂'s conduction band. Then excited chlorophyll molecules are converted into cations and interact with methyl orange molecules. Eventually, it was turned into an uncharged chlorophyll molecule, and the process repeats.

4. Conclusion

In this study, [BMIM]BF₄-chlorophyll sensitized TiO₂ catalyst was successfully prepared and performed excellent degradation efficiency. The optimum preparation condition is: the ratio of [BMIM]BF₄ and tetrabutyl titanate is 3:13, 40 ppm chlorophyll, pH of tetrabutyl titanate mixing solution is 6; IL-TiO₂ is calcined at 180 °C for 10 h, and sensitized at 25 °C for 24 h.

Under ultraviolet light irradiation, the ratio of [BMIM]BF₄ to tetrabutyl titanate is 3:13 and without chlorophyll, the degradation rate is 88.43%. Under visible light irradiation, when the chlorophyll concentration is 40 ppm, the ratio of [BMIM]BF₄ to tetrabutyl titanate is 3:13, the degradation rate of methyl orange reached the highest point of 79.80%.

Through XRD analysis, the positions of three groups of diffraction peaks are similar, it can be seen that the addition of ionic liquid and chlorophyll will not change the crystal structure.

According to FT-IR analysis, it can be seen that the addition of chlorophyll, which is physical adsorption on the surface, and ionic liquid can changed the type and structure of functional groups of the catalyst.

Nitrogen adsorption-desorption analysis shows that the specific surface area of IL-TiO₂ increases, the pore size decreases, and the pore volume basically is unchanged, confirming that the modified catalyst has better degradation ability.

5. Innovations

In this study, novel [BMIM]BF₄-chlorophyll sensitized TiO₂ catalysts prepared by hydrothermal synthesis method was developed. By using [BMIM]BF₄ and chlorophyll, catalysts with a high specific surface area and visible light response were formed. Moreover, the effects of ratio of [BMIM]BF₄ to tetrabutyl titanate and the concentration of chlorophyll on the degradation rate were clarified. Eventually, we procured the best condition of synthesized catalysts, and the research offers a scientific alternative for degrading waste-water under visible light condition.

6. Prospect

Further experimental tests about other factors we need to analyze whether they effect the degradation rate, such as pH of the solution in hydro-thermal synthesis method, sensitization temperature and time in preparing IL-chlorophyll-TiO₂ catalysts. Additionally, we need to ensure this catalyst can degrade other organic, toxic degradants or impurities of great quantities in reality.

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Acknowledgments

The authors would like to appreciate the guidance of professor Chunshan Li who instructed the study; he is our off-school instructor from *Institute of process engineering, Chinese Academy of Sciences*. Our sincere thanks also go to Chunshan Li's research group members of MMA-Yu Chen and Hui Zhou and *Beijing National Day School's* teacher Weilin Xin for teaching us professional laboratory process, providing facilities and instruments and offering valuable feedback of paper. Their dynamism and motivations have deeply inspired us. They have taught us the methods to accomplish the research and to present the research works. This research was financially supported by *Beijing Key Laboratory of Ionic Liquids Clean Process of Institute of process engineering*. All guidance provided by the teacher is unpaid.

Xutao Mao carried out the characterization analyses of catalyst and degradation experiments for methyl orange. Zichu Wang contributed mainly in preparation of catalysts and wrote the paper. All authors discussed, reviewed and revised the paper.