

ORIGINAL RESEARCH ARTICLE

Surface modification of nano-TiO₂ with lanthanide-acetylacetonate complexes

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ABSTRACT

The surface modification of nano-TiO₂ was carried out with lanthanide-acetylacetonate complexes by adsorption method. The effects of lanthanide complexes content, lanthanide element type, adsorption temperature, solvent dosage, adsorption time and other conditions on the photodegradation activity of methyl orange by the modified catalyst were studied, and suitable modification conditions were obtained. The results show that the photocatalytic activity of the modified nano-TiO₂ is much higher than that of the unmodified pure TiO₂, and the lanthanide-acetylacetonate complexes is an excellent surface modifier.

Keywords: TiO₂; Lanthanide; Acetylacetonate; Surface Modification; Degradation

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1. Introduction

Nano-titanium dioxide (TiO₂) has good visible light transmittance, strong ultraviolet light absorption performance, and high chemical activity. It has attractive application prospects in solar energy storage and utilization, photocatalytic conversion, environmental treatment of oxidative degradation of organic pollutants, and the preparation of new materials. The production of nano-TiO₂ has gradually realized industrialization, but due to the small size and high surface energy of nano-particles, it is easy to agglomerate between the particles, which seriously affect its performance. At the same time, nano-TiO₂ is a strong polar substance, which is not easy to disperse in organic systems (such as coatings, plastics, etc.) and greatly limits its application range. In order to make full use of the excellent properties of nano-TiO₂, it is necessary to use suitable reagents to improve the surface properties of TiO₂. On the one hand, it can effectively prevent the agglomeration of nanoparticles; on the other hand, it has no obvious adverse effect on the properties of nanoparticles. The ideal modification can even improve and promote the properties of nanoparticles. The advantage of this method is that there is no damage to the structure and size of the nanoparticle matrix, and the result is good in reproducibility, which is conducive to mass production. There have been many reports on the surface modification of nano-TiO₂ by inorganic matter^[1,2] or organic matter^[3,4].

Due to the high band gap of TiO₂ (up to 3.2 eV), only ultraviolet light with a wavelength less than 387.5 nm can excite its catalytic activity, while the energy spectrum of ground sunlight is mainly distributed in the visible and near-infrared regions, with only a small amount

(around 3%) of the light is distributed in the ultraviolet region. In order to replace the expensive and fragile artificial ultraviolet light system with the abundant available solar energy resources, it is expected that through the modification of TiO_2 , the effective excitation will be transferred from the ultraviolet region to the visible light region. Experimental studies have shown that nano- TiO_2 particles are doped with precious metal elements (Pt, Pd, etc.)^[5,6], transition metal ions (Fe^{3+} , Ru^{3+} , Re^{5+} , etc.)^[7,8], non-metal elements (N, S, C, halogen, etc.)^[9-11], etc. can reduce the band gap energy level to a certain extent, and achieve visible light excitation. It is worth noting that people have also found that surface modification of TiO_2 with dye molecules (so-called dye sensitization) can greatly increase the utilization rate of visible light absorption^[12-14].

Based on the above background, consider the use of lanthanide-acetylacetonate complexes to modify the surface of TiO_2 . (1) Because lanthanide-acetylacetonate complexes are insoluble in water, but can be dissolved in many organic solvents, the modification with it should improve the lipophilic property of the surface of TiO_2 . (2) The complex contains lanthanide metal ions and organic groups, which have both inorganic and organic properties, and should be able to act as a good dispersant to prevent agglomeration between nanoparticles. (3) Dye sensitization refers to the excited state electrons generated by dye molecules absorbing visible light or even near-infrared light, which are directly injected into the conduction band of TiO_2 nanocrystals through interface electron transfer, thereby broadening the wavelength range of excitation light. Lanthanide-acetylacetonate complexes have good fluorescence properties^[15-18]. Whether it can act like a photosensitizer is an interesting question. The currently reported photosensitizers mainly include metal ruthenium bipyridine complex series, metal osmium bipyridine complex series, phthalocyanine and cyanine series, porphyrin series, chlorophyll and its derivatives, etc.^[19,20]. The photosensitization of lanthanide-acetylacetonate complexes has not been reported yet. (4) If the metal complexes modify the surface of nano-

TiO_2 , the performance of nano- TiO_2 changes significantly, then it is possible to achieve such control by adjusting the electronic and steric effects of the ligand and the types of metal atoms, so as to control the performance of metal complexes, and further control the performance of modified nanoparticles. Research in this area is still lacking. At the same time, researchers have also noticed that the doping of lanthanide ions also has a certain promotion effect on the photoactivity of TiO_2 ^[21-23]. Based on the synthesis of lanthanide-acetylacetonate complexes, the author modified the surface of nano- TiO_2 , and used the photocatalytic degradation of methyl orange as a probe reaction to study the appropriate conditions for the surface modification of nano- TiO_2 .

2. Experiment

Nano- TiO_2 , Zhejiang Wanjing New Material Co., Ltd., particle size 10–20 nm, specific surface area $60\text{--}70\text{ m}^2\cdot\text{g}^{-1}$, purity $\geq 99.0\%$, vacuum dried at $45\text{ }^\circ\text{C}$ for 1 d, and then placed in a desiccator for later use. La_2O_3 , Sm_2O_3 , Er_2O_3 , purity $>99.0\%$, produced by Shanghai Yuelong Non-ferrous Metals Co., Ltd. $\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$, hydrochloric acid, sodium hydroxide, acetylacetonate, and absolute ethanol are all analytical reagents.

Ultrasonic cleaner, KQ-50E, Kun Shan Ultrasonic Instruments Co., Ltd. Magnetic stirrer, type 78-1, Shanghai Jingfeng Instrument Co., Ltd. Vacuum drying oven, model ZK-82B, Shanghai Shiyuan Instrument Factory Co., Ltd. UV lamp, ACTINIC BL 20 W, PHILIPS, imported from Poland. UV lamp, ACTINIC BL 40 W, PHILIPS, imported from the Netherlands. Centrifuge, Model 800, Shanghai Jingfeng Instrument Co., Ltd. Spectrophotometer, Model 721, Shanghai No.3 Instrument Analysis Factory.

2.1 Synthesis of $\text{Ln}(\text{acac})_3$ ($\text{Ln} = \text{La}, \text{Ce}, \text{Sm}, \text{Er}$)

The synthesis of $\text{Ln}(\text{acac})_3$ was carried out via references^[24,25]. Taking $\text{La}(\text{acac})_3$ as an example: weigh La_2O_3 white powder (3.00 g, 9.21 mmol) in a small beaker, add a small amount of

water, start magnetic stirring, slowly add concentrated hydrochloric acid dropwise, then the white powder gradually dissolves into a colorless solution. Add 5.7 mL (55.6 mmol) of acetylacetonate to form two phases of oil and water, and then add about 6 mL of industrial alcohol to form a homogeneous phase. Slowly add NaOH solution dropwise to the above solution, the reaction solution gradually produces a white precipitate, dripping until the pH value of the mixed solution is 6.5, at this time the reaction solution is a thicker solid-liquid mixture. After suction filtration, the filter cake was thoroughly washed with distilled water and dried in vacuum at 45 °C for 2 d to obtain a white solid $\text{La}(\text{acac})_3 \cdot 2\text{H}_2\text{O}$ (6.86 g, 79.0%).

$\text{Sm}(\text{acac})_3 \cdot 2\text{H}_2\text{O}$ and $\text{Er}(\text{acac})_3 \cdot 3\text{H}_2\text{O}$ were synthesized from Sm_2O_3 and Er_2O_3 , respectively, according to the above-mentioned similar methods, and the yields were 78.1% and 64.5%, respectively. $\text{Ce}(\text{acac})_3 \cdot 2\text{H}_2\text{O}$ was synthesized from $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ by a similar method, and the yield was 54.6%.

2.2 Synthesis of $\text{Ce}(\text{acac})_4$ ^[26]

Weigh $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ red solid (9.45 g, 17.23 mmol) in a small beaker, add about 45 mL of water to dissolve, add 7.1 mL (69.0 mmol) of acetylacetonate to form a two-phase oil and water, then add about 7 mL industrial alcohol, stir to form a homogeneous colorless solution, at this time the pH value is about 1. The aqueous ammonia solution was gradually added dropwise to the above solution, and a yellow precipitate was gradually produced in the reaction solution. When the pH of the solution reached 5, the suspension appeared light green. When the pH value of the mixed solution reaches 6.5, stop adding ammonia water, continue to stir for 0.5 h, then suction filter, the filter cake is fully washed with distilled water, and vacuum dried at 45 °C for 2 d, a brown-yellow $\text{Ce}(\text{acac})_4$ solid (3.93 g, 42.5%) gained.

2.3 Modification of nano- TiO_2

The typical modification process is as follows: weigh about 2 g of nano- TiO_2 in a

round bottom flask, then weigh in the required quality of lanthanide-acetylacetonate complexes, add a set volume of absolute ethanol, magnetically stir for 0.5 h, then ultrasonic treatment for 20 min. And then placed in a constant temperature oil bath with a set temperature and agitated for a certain period of time. Take it out, centrifuge the mixed solution, discard the solvent, wash the precipitate with distilled water and centrifuge, after repetition for once, finally transfer the precipitate to a watch glass and dry it under vacuum at 45 °C for 1 d, then take it out and place it in a desiccator for later use.

2.4 Photocatalytic degradation

Weigh 0.100 g of the photocatalyst into a 100 mL beaker, add 50 mL of a methyl orange solution with an initial concentration of $16.7 \text{ mg} \cdot \text{L}^{-1}$, start magnetic stirring, and place the suspension mixture under a 20 W ultraviolet lamp (the tube is 20 cm away from the liquid surface) after irradiation for a certain period of time, samples were taken, centrifuged to remove solid particles, and the clear liquid was measured with a spectrophotometer to measure the absorbance at 462 nm of the solution. According to the standard curve equation of absorbance and concentration, the concentration of methyl orange solution in each period is calculated and determined, so as to know the conversion rate of methyl orange^[27].

3. Results and discussion

3.1 The relative ratio of lanthanide complexes and TiO_2

The relative ratio of lanthanide complexes to TiO_2 is the most direct factor affecting the modification effect. If the amount of lanthanide complexes is too low, the surface of the TiO_2 particles will be limited, and the properties of particle aggregation and surface wettability cannot be effectively improved. If the amount of lanthanide complexes is too high, the surface of the nanoparticles will be completely covered by the lanthanide complexes, and the photocatalytic ability of TiO_2 will not be able to play well. Therefore,

there should be an optimal ratio between lanthanide complexes and TiO₂. **Table 1** shows the photocatalytic activity of modified TiO₂ when the ratio of La(acac)₃ to TiO₂ is different. When $w[\text{La}(\text{acac})_3/\text{TiO}_2] \geq 3\%$, the activity of modified TiO₂ is worse than pure TiO₂. When

$w[\text{La}(\text{acac})_3/\text{TiO}_2] = 0.25\%$, the photoactivity of the modified catalyst is the best. After the modification of nano-TiO₂, the activity has been significantly improved, indicating that the modification of lanthanide complexes has played a positive role.

Table 1. The relationship between photocatalytic degradation rate and time under different mass ratios of La(acac)₃ and TiO₂ (%)

Time/min	0	20	40	60	80	100	120	140	160	180	
	0	0	10.3	19.8	26.8	33.6	37.4	44.6	52.7	59.7	69.0
	0.25	0	22.9	37.0	47.5	58.8	69.2	79.6	87.9	91.6	92.5
	0.5	0	21.2	35.1	43.5	53.4	64.8	74.9	84.2	91.9	94.4
$w[\text{La}(\text{acac})_3/\text{TiO}_2]/\%$	0.75	0	14.8	30.0	36.1	47.5	56.2	64.2	72.7	77.3	88.1
	1	0	13.4	25.5	31.0	39.0	47.0	54.0	63.4	73.4	82.5
	3	0	4.5	11.3	15.8	22.9	33.0	35.5	49.1	59.7	71.6
	5	0	4.1	5.0	11.4	20.5	28.0	32.8	43.0	49.4	57.1

Modification conditions: 70 °C, 2.5 h, ethanol/TiO₂ = 29 mL·g⁻¹.

3.2 Impact of lanthanide species

There are many types of lanthanide elements, and the author chooses La³⁺, Ce³⁺, Ce⁴⁺, Sm³⁺, and Er³⁺ for research. From the perspective of electronic structure and luminescence ability^[28], La³⁺(4f⁰) has no 4f electrons, so there is no f-f energy level transition, which belongs to lanthanide ions that do not emit light in the visible region; the transition energy frequency f-f of Sm³⁺(4f⁵) between the lowest excited state and the ground state falls in the visible region, and the transition energy of f-f electron is moderate, which belongs to the lanthanide ion with strong luminescence; the energy difference between the lowest excited state and ground state of Er³⁺(4f¹¹) is small, the energy level is dense, and the probability of non-radiative transition is high, which is a lanthanide ion with very weak luminescence;

Ce³⁺ is a low-valent ion with f-d transition; Ce⁴⁺ is one of the few tetravalent ions. The comparison of Ce³⁺ and Ce⁴⁺ can reflect the influence of lanthanide valence changes.

The experimental results are shown in **Table 2**. After the Ce³⁺ and Ce⁴⁺ complexes are modified, the activity of the nanoparticles is very low, while the La³⁺, Sm³⁺, and Er³⁺ complexes have the same activity of the photocatalyst after modification. This seems to mean that the activity of the photocatalyst is not directly related to the electronic structure of the lanthanide ions, but there is some indirect connection. In the next step, the author will analyze and compare the luminescence properties of lanthanide complexes, and investigate the intrinsic relationship between these properties and the photocatalyst activity.

Table 2. The relationship between photocatalytic degradation rate of different lanthanide ions and time (%)

Time/min	0	20	40	60	80	100	120	140	160
La ³⁺	0	22.9	37.0	47.5	58.8	69.2	79.6	87.9	91.6
Ce ³⁺	0	7.2	12.1	20.5	28.0	34.4	41.7	49.4	63.2
Sm ³⁺	0	22.2	32.7	50.1	58.6	70.5	79.0	87.1	91.8
Er ³⁺	0	19.3	28.3	46.4	57.7	68.2	77.7	86.6	91.0
Ce ⁴⁺	0	9.3	19.3	27.2	34.0	40.9	47.6	55.2	62.3

Modification conditions: $w[\text{Ln}(\text{acac})_3/\text{TiO}_2] = 0.25\%$, 70 °C, 2.5 h, ethanol/TiO₂ = 29 mL·g⁻¹.

3.3 Influence of adsorption temperature

The adsorption of nanoparticles to the complex solution is a complex physical and chemical process. Physical adsorption and chemical adsorption can occur successively or simultaneously in the same system due to different condi-

tions^[29]. The adsorption temperature has a great and complicated influence on the adsorption process. Because adsorption is an exothermic process, as long as the adsorption has reached equilibrium, the amount of adsorption will decrease regardless of physical adsorption or chemical adsorption when the temperature is in-

creased. However, because the chemical adsorption often does not reach equilibrium at low temperatures, increasing the temperature will accelerate the adsorption rate. Therefore, for chemical adsorption at low temperatures, the adsorption capacity will rise with the increase in

temperature. Until the equilibrium is truly reached, the adsorption capacity will decrease with the increase in temperature. **Table 3** shows that the modified catalyst has the best activity when the adsorption temperature is 50 °C.

Table 3. The relationship between photocatalytic degradation rate and time at different temperatures (%)

Time/min	0	20	40	60	80	100	120	140	160	
Temperature °C	20	0	23.0	34.8	43.9	53.4	61.6	69.5	78.4	85.7
	50	0	28.8	45.4	58.3	73.9	79.4			
	70	0	22.9	37.0	47.5	58.8	69.2	79.6	87.9	91.6

Modification conditions: $w[\text{La}(\text{acac})_3/\text{TiO}_2] = 0.25\%$, 3.5 h, ethanol/ $\text{TiO}_2 = 29 \text{ mL} \cdot \text{g}^{-1}$.

3.4 The influence of solvent dosage

The amount of solvent will affect the concentration of the complex solution and the relative ratio of liquid (solvent) to solid (TiO_2). When nano- TiO_2 is adsorbed in the solution, in addition to adsorbing the complex solute, it also adsorbs the solvent ethanol, so the interaction between the components must also be con-

sidered. The experimental results of the three liquid-solid ratios show that the modification effect is best when the solvent dosage is kept at ethanol/ $\text{TiO}_2 = 29 \text{ mL} \cdot \text{g}^{-1}$. Too much or too little amount of solvent will lead to reduced activity of the modified catalyst. The experimental results are shown in **Table 4**.

Table 4. The relationship between photocatalytic degradation rate and time in different ratios of solvent and TiO_2 (%)

Time/min	0	20	40	60	80	100	120	140
40 $\text{mL} \cdot \text{g}^{-1}$	0	23.0	36.0	49.2	57.2	65.7	73.5	83.8
29 $\text{mL} \cdot \text{g}^{-1}$	0	28.8	45.4	58.3	73.9	79.4		
20 $\text{mL} \cdot \text{g}^{-1}$	0	22.4	38.6	41.3	53.6	63.9	75.6	81.8

Modification conditions: $w[\text{La}(\text{acac})_3/\text{TiO}_2] = 0.25\%$, 50 °C, 3.5 h.

3.5 The effect of adsorption time

The longer is the adsorption time, the closer the adsorption is to equilibrium. Mastering the adsorption equilibrium time can avoid wasting modification time and improve the efficiency of the modification process. It can be seen from **Ta-**

ble 5 that when the adsorption time is extended from 0.5 h to 1 h at 50 °C, the photocatalytic conversion rate is significantly improved. If the adsorption time is extended, the photocatalytic activity has not changed much, so the adsorption time should be set at 1 h.

Table 5. The relationship between photocatalytic degradation rate and time for different adsorption time (%)

Time/min	0	20	40	60	80	100	120	
Adsorption time/h	0.5	0	22.1	39.7	51.9	67.3	78.2	88.5
	1.0	0	25.3	45.3	60.0	70.4	80.3	89.9
	3.5	0	28.8	45.4	58.3	73.9	79.4	

Modification conditions: $w[\text{La}(\text{acac})_3/\text{TiO}_2] = 0.25\%$, 50 °C, ethanol/ $\text{TiO}_2 = 29 \text{ mL} \cdot \text{g}^{-1}$.

3.6 Light source

The above studies show that under ultraviolet light conditions, the photocatalytic activity of TiO_2 suitably modified by the lanthanide-acetylacetonate complexes is greatly improved, so under ordinary light conditions, does the modified catalyst still have this advantage? For this reason, the author investigated the cata-

lytic degradation under the condition with a 200 W incandescent lamp, and the results are shown in **Figure 1**. It can be seen from **Figure 1** that the photoactivity of the modified catalyst is significantly higher than that of unmodified pure TiO_2 .

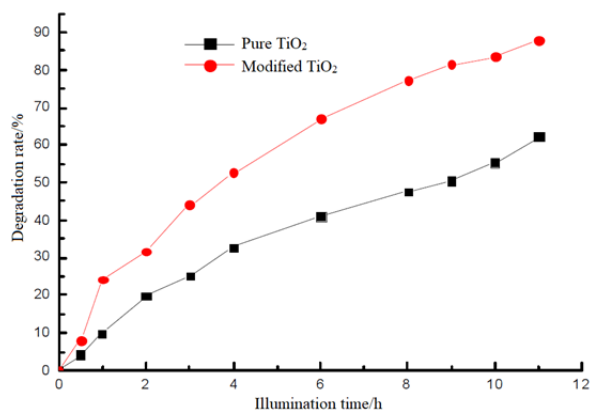


Figure 1. Photocatalysis under 200 W incandescent lamp illumination.

Modification conditions: $w[\text{La}(\text{acac})_3/\text{TiO}_2] = 0.25\%$, $50\text{ }^\circ\text{C}$, 1 h, $\text{ethanol}/\text{TiO}_2 = 29\text{ mL}\cdot\text{g}^{-1}$.

4. Conclusion

The surface modification of nano-TiO₂ with lanthanide-acetylacetonate complexes was used for the first time, and the effect of modification conditions on the photocatalytic activity was studied. The results show that the photocatalytic activity of the modified nano-TiO₂ can be significantly improved no matter under the conditions of ultraviolet light or ordinary incandescent lamp. The specific reasons for the increased photoactivity of the modified catalyst need to be further studied.

Conflict of interest

The authors declare that they have no conflict of interest.

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