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Preparation and Properties of CaCO₃-Supported Nano-TiO₂ Composite with Improved Photocatalytic Performance

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Abstract: In order to improve the photocatalytic degradation efficiency of nano-TiO₂, reduce its usage and realize recycling and reuse, $CaCO_3$ -TiO₂ composite photocatalyst was prepared with calcium carbonate (CaCO₃) and TiO₂ in a grinding machine through the integration of grinding depolymerization, dispersion and particle composition. The photocatalytic degradation performance, recycling performance, structure and morphology of CaCO₃-TiO₂ were studied. The interaction mechanism between CaCO₃ and TiO₂ and the improvement mechanism for the photocatalytic performance of TiO₂ were also discussed. The results show that under the UV light irradiation for 20 and 40 min, the degradation efficiency of methyl orange by the composite photocatalyst with 40% TiO₂ (mass fraction) was 90% and 100%, respectively. This was similar to that of pure TiO₂, and the performance of the composite photocatalyst was almost unchanged after five cycles. CaCO₃-TiO₂ is formed by the uniform loading of nano-TiO₂ particles on the CaCO₃ surface, and the nano-TiO₂ particles are well dispersed. Due to the facts that the dispersion of nano-TiO₂ is improved in the presence of CaCO₃ and TiO₂, the formation of this complex is an intrinsic mechanism to improve the photocatalytic efficiency of nano-TiO₂ and reduce its usage in application processes.

Keywords: CaCO₃-TiO₂; composite particle; photocatalytic performance; recycling

1. Introduction

In recent decades, with the rapid development of industries such as chemical industry, mining industry and agricultural breeding industry, environmental pollution problems, including water pollution, have become increasingly serious. Photocatalytic techniques are considered to be one of the most ideal ways to combat environmental pollution problems such as water pollution [1,2]. Therefore, it is of great significance to optimize the use conditions of photocatalysts, improving the function of photocatalyst technology and reducing the use amount of photocatalyst required to reduce the overall cost. Nano-TiO₂ has become the most widely studied and applied semiconductor photocatalytic materials owing to its non-toxic, non-polluting and stable properties [3,4]. Under the excitation of ultraviolet light, electron–hole pairs are produced by electron transition in nano-TiO₂, following which the separated electrons and holes migrate to the surface of TiO₂ to produce active groups or directly react with pollutants. Thus, the degradation of pollutants such as dyes, heavy metal ions, phenols, dichlorophenol and antibiotics can be achieved through the further redox action [5–8]. However,



there are still the several problems in the application of TiO₂. Firstly, nano-TiO₂ is easily agglomerated due to its high surface energy, which leads to the reduction of specific surface area and surface active sites, thus reducing its photocatalytic activity. Secondly, the loss of nano-TiO₂ is serious when it is used in water, and is difficult to recover. The loss of nano-TiO₂, caused by the lack of reuse, not only increases the use cost but also causes secondary pollution [9,10]. Many studies have shown that loading nano-TiO₂ on the surface of the carrier with a large particle size to prepare a composite photocatalyst can effectively solve the above problems [11–13]. At present, the carriers for nano-TiO₂ are mostly natural minerals and inorganic materials such as glass and ceramics. Among them, the natural mineral carriers that have been greatly studied are diatomite, zeolite, kaolin and montmorillonite [14–17]. However, these minerals generally need to be processed, such as via ore dressing and purification,

to meet the requirements for catalyst carriers. This increases the cost of the composite photocatalyst,

which undoubtedly restricts their industrial production and application. Calcium carbonate (CaCO₃) is an important inorganic mineral material, mainly made of non-metallic mineral raw materials such as calcite. It has the characteristics of high purity, high whiteness and low cost, and is obviously superior to most non-metallic minerals in cost-performance [18,19]. Therefore, the construction of CaCO₃-nano-TiO₂ composite photocatalyst using $CaCO_3$ as a carrier can not only improve the recyclability and reusability performance of nano-TiO₂, but also improve the photocatalytic efficiency of nano-TiO₂ particles through loading to reduce the agglomeration of TiO₂ particles. Meanwhile, the efficient utilization of CaCO₃ mineral can be achieved by increasing its added value. Generally, TiO₂-loaded mineral composite particles can be prepared by hydrolytic deposition, sol-gel and mechanical grinding methods. Sun et al. used purified diatomite as the carrier and prepared diatomite-nano-TiO₂ composite photocatalyst by the hydrolysis of TiCl₄ on its surface and the calcination of the product [20]. The maximum photocatalytic degradation efficiency of Rhodamine B (10 ppm) reached up to around 95% within 20 min of irradiation. Kun et al. prepared montmorillonite–nano-TiO₂ composite photocatalyst by the sol-gel method with montmorillonite as the carrier [21]. The specific conversion of contaminant by the composite is three times that of TiO_2 . As for the loading of TiO_2 on CaCO₃, Tanabe [22] prepared CaCO₃–TiO₂ composite particles through carbonation in a TiO₂ system. Sun [23] prepared CaCO₃–TiO₂ composite particles by the hydrophobic agglomeration method. However, these methods are complex and costly. Sun et al. prepared CaCO₃-TiO₂ composite pigment by liquid phase mechanical chemistry with CaCO₃ as the carrier. However, this process requires a large amount of water, and subsequent processes such as filtration and drying are also required, which are complicated and consume more energy. Therefore, in this study, grinding depolymerization, dispersion and particle composition were integrated; the CaCO₃-TiO₂ composite photocatalyst was prepared by directly dry grinding CaCO₃ and nano-TiO₂ powder in a grinding machine, which has the advantages of requiring a simple process and low cost. In this study, the preparation conditions of the $CaCO_3$ -TiO₂ composite photocatalyst were optimized. The morphology and structure of CaCO₃–TiO₂ composite particles were characterized and the photocatalytic degradation of CaCO₃-TiO₂ was carried out. The photocatalytic degradation of methyl orange by CaCO₃–TiO₂, including its reusability, was tested. Moreover, the combination mechanism between $CaCO_3$ and TiO_2 and the improvement mechanism for the photocatalytic performance of nano-TiO₂ were discussed.

2. Methods

2.1. Raw Materials and Reagents

The CaCO₃ raw material was calcite grinding powder produced in Jilin province, China, with a purity of 100% and whiteness of 95%. The D₉₇ (particles with size ranging from 0 to D₉₇ account for 97% of the weight ratio) of the used CaCO₃ was 25 μ m, 15 μ m and 10 μ m. The raw material of nano-TiO₂ used in this study was the commercial degussa P₂₅ product, which is composed of the mixed phase of anatase and rutile.

2.2. Preparation of CaCO₃–TiO₂ Composite Photocatalyst

According to the composite ratio, a certain amount of nano-TiO₂ powder and CaCO₃ powder with specific particle sizes were put into an oven and dried at 80 °C for 2 h. Then, the nano-TiO₂ powder and CaCO₃ powder were well mixed, and the mixed powder was added to an RK/XPM- Φ 120 grinding machine. After grinding for 30 min (the diameter of grinding bowl was 120 mm, the speed was 9 r/min and the speed of the grinding rod was 220 r/min), the CaCO₃–nano-TiO₂ composite photocatalyst was obtained.

2.3. Photocatalytic Properties Test

The photocatalytic performance of $CaCO_3$ –TiO₂ composite photocatalyst was tested with methyl orange as the target degradation product. A 300 W mercury lamp with a dominant wavelength of 254 nm was used as the light source. First, 50 mg of $CaCO_3$ –TiO₂ composite photocatalyst was added to 50 mL of as-prepared methyl orange solution (the concentration was marked as C₀, 10 mg/L) to obtain a suspension. In order to reduce the measurement error caused by sample adsorption, dark reaction was carried out for 1 h. After turning on the light source, the residual concentration of methyl orange was tested at specified intervals and marked as C. The photocatalytic degradation performance of the samples was characterized and evaluated by the change of C/C_0 . Linear regression was performed on the relationship between –Ln (C/C_0) and t (lighting time), and the linear slope was used to characterize the photocatalytic degradation rate.

The measurement of the concentration of methyl orange solution after photodegradation was as follows: the solution was centrifugated, the supernatant was removed and its absorbance was measured by a UV-VIS spectrophotometer (Cary 5000, Varian company, Palo Alto, CA, USA). The concentration of methyl orange in the solution was obtained through the relationship between the absorbance and concentration.

After the photocatalytic degradation of methyl orange, the suspension was centrifuged to obtain the sediments (photocatalyst). After being dried at a low temperature, the composite photocatalyst was tested for the photocatalytic degradation performance again, which was regarded as one cycle. The above process was repeated multiple times to obtain the cycle degradation performance of the samples.

2.4. Characterization

An X-ray powder diffractometer (D/MAX2000, Rigaku Corporation, Tokyo, Japan) was used to analyze the phase composition of the $CaCO_3$ –TiO₂ composite photocatalyst. A scanning electron microscope (SEM, S-3500N, HITACHI, Tokyo, Japan) was used to observe the sample morphology. The UV-VIS diffuse reflection absorption spectrum (Cary 5000, USA Varian, Palo Alto City, CA, USA) was used to characterize the light absorption properties of the samples. Fourier transform infrared spectroscopy (Spectrum 100, PerkinElmer Instruments (Shanghai) Co., Ltd., Shanghai, China) was used to test the binding properties of $CaCO_3$ and TiO₂.

3. Results and Discussion

3.1. Photocatalytic Degradation of Methyl Orange by CaCO₃–TiO₂

3.1.1. Effect of Particle Size of CaCO₃

In order to investigate the effect of the particle size of CaCO₃ on the properties of the prepared CaCO₃–TiO₂ composite photocatalyst, CaCO₃–TiO₂ composite photocatalysts were prepared with 25 μ m, 15 μ m and 10 μ m CaCO₃ as the carrier (the mass ratio of nano-TiO₂ was 40%). Figure 1 shows the photocatalytic degradation of methyl orange by CaCO₃–TiO₂ and pure TiO₂, and a blank experiment was also conducted. It can be seen that when the pure methyl orange solution was illuminated by the ultraviolet light only, the C/C₀ remained almost unchanged with the increase of illumination time, indicating that there was no degradation effect on the methyl orange. By contrast,

treatment with the CaCO₃–TiO₂ composite photocatalyst (the size of CaCO₃ was 15 μ m) and pure TiO₂ both resulted in the effective degradation of methyl orange. After 30 min of irradiation, the C/C₀ was reduced to less than 0.05, indicating that the degradation efficiency was higher than 95%; after 40 min of irradiation, the degradation efficiency reached 100%. Obviously, CaCO₃–TiO₂ has excellent photocatalytic performance, which is similar to that of nano-TiO₂. Since the mass ratio of TiO₂ to CaCO₃–TiO₂ was only 40%, the above results indicate that CaCO₃ has an improving effect on the performance of TiO₂.

Figure 1 also shows that among the three CaCO₃–TiO₂ samples, the composite with 15 μ m CaCO₃ as the carrier exhibited the highest degradation efficiency. After 20 min of irradiation, the degradation efficiency of methyl orange was 90%, and the samples with 25 μ m and 10 μ m CaCO₃ as the carrier only reached about 82%. When the irradiation time increased to 30 min, the methyl orange degradation efficiencies of the three samples were 98%, 86% and 89%, respectively. The above results indicate that the particle size and specific surface area of CaCO₃ are important, and that CaCO₃ with a particle size of 15 μ m properly matched with the nanoTiO₂ particles to form an optimal composite relationship. Therefore, CaCO₃ with a particle size of 15 μ m was chosen as the carrier to be compounded with nano-TiO₂.



Figure 1. Effect of the particle size of CaCO₃ on the performance of the composite photocatalyst.

3.1.2. Effect of Loading Amount of Nano-TiO₂

As the photocatalytic active component in CaCO₃–TiO₂, the loading amount of nano-TiO₂ should have a significant effect on the performance of the composite photocatalyst. Therefore, using 15 μ m CaCO₃ as the carrier, CaCO₃–TiO₂ composite photocatalysts with different mass ratios of nano-TiO₂ were prepared, and the degradation performance of methyl orange under ultraviolet light was tested. The results are shown in Figure 2. As the mass ratio of nano-TiO₂ increased from 10% to 40%, the degradation efficiency of CaCO₃–TiO₂ increased gradually. When the composite photocatalyst with a TiO₂ mass ratio of 40% was illuminated for 20 min, the C/C₀ was lower than 0.1, indicating that the degradation efficiency reached higher than 90%. And when the irradiation time increased to 40 min, the degradation efficiency reached 100%, which is equivalent to pure TiO₂. When the mass ratio of nano-TiO₂ increased to 50%, although the degradation efficiency was improved after 10 min of illumination, the degradation efficiency remained almost unchanged when the irradiation time was extended, with a maximum of only 90%. Obviously, the mass ratio of nano-TiO₂ in CaCO₃–TiO₂ should be set as 40%. Since $CaCO_3$ -TiO₂ with only a small mass ratio of nano-TiO₂ reaches the photocatalytic degradation effect similar to that of pure nano-TiO₂, the use amount of TiO₂ can be significantly reduced and thus cost can be saved in practical applications. This is a result of the significant improvement in the photocatalytic efficiency of TiO₂ by its combination with CaCO₃. It is speculated that this improvement results from the improvement of the dispersibility of nano-TiO₂ and the formation of a combination interface between TiO₂ and CaCO₃.



Figure 2. Effect of mass ratio of TiO_2 on the properties of the composite photocatalyst.

3.1.3. Photocatalytic Degradation of Different Concentrations of Methyl Orange Solution by CaCO_3–TiO_2

The investigation of the degradation performance of $CaCO_3$ -TiO₂ in different concentrations of methyl orange solution can not only further verify the photocatalytic degradation ability of $CaCO_3$ -TiO₂, but it can also determine its reasonable scope of application. Figure 3 shows the photocatalytic degradation effect of CaCO₃-TiO₂ for different concentrations of methyl orange solution. It can be seen that the degradation efficiency of the $CaCO_3$ -TiO₂ composite photocatalyst on each concentration of methyl orange solution increased with the increase of the illumination time, and finally reached a higher degradation effect. Comparing the degradation effect of different concentrations, it was found that the degradation efficiency of methyl orange solution with concentrations of 10 and 20 ppm by $CaCO_3$ -TiO₂ was higher than that of concentrations of 50 and 80 ppm. Among them, the methyl orange solution with concentrations of 10 and 20 ppm could be completely degraded ($C/C_0 = 0$) by CaCO₃–TiO₂ at illumination times of 60 and 80 min, respectively, and the degradation rate was faster. In contrast, the degradation rates of 50 and 80 ppm methyl orange solution by CaCO₃–TiO₂ were reduced, and the degradation efficiencies were 90% and 80%, respectively (C/C₀ was 0.1 and 0.2, respectively) at illumination times of 60 and 90 min. These results show that the CaCO₃-TiO₂ composite photocatalyst can effectively degrade methyl orange solution with concentrations of 10-80 ppm. The reason why the degradation rate decreases with the increasing concentration of methyl orange solution is that high concentrations of pollutants require longer reaction times.



Figure 3. Effect of the concentration of methyl orange solution on the degradation efficiency (**a**) and degradation rate (**b**) of $CaCO_3$ -TiO₂ composite photocatalyst.

3.1.4. Recycling Performance of CaCO₃–TiO₂ Composite Photocatalyst

The recycling performance of the catalyst is an important factor reflecting its stability and practical application performance. Therefore, we investigated the recycling performance of the optimum CaCO₃–TiO₂ composite photocatalyst (the particle size of CaCO₃ was 15 μ m, the mass ratio of TiO₂ was 40%). The results are shown in Figure 4. The results show that the photocatalytic degradation performance of CaCO₃–TiO₂ after five cycles is similar to that of the first use, indicating that recycling does not reduce its performance. This indicates that the CaCO₃–TiO₂ composite photocatalyst prepared in this study has excellent recycling performance and can be recycled and reused several times, thereby reducing the cost. Obviously, this is due to the loading of TiO₂ on the surface of CaCO₃, which results in the nano-TiO₂ being firmly fixed on the surface of CaCO₃. Therefore, the loss of TiO₂ is prevented, and CaCO₃–TiO₂ can easily be separated from water due to its large particle size. However, single nano-TiO₂ particles have a small particle size, so they are difficult to precipitate and easily lost when separated from their carrier. Therefore, it is believed that the CaCO₃–TiO₂ composite photocatalyst has practical application prospects for sewage treatment.



Figure 4. Cyclic curve of the degradation of methyl orange by CaCO₃-TiO₂ composite photocatalyst.

3.2. Optical Performance Test

Figure 5 shows the UV-VIS diffuse reflectance absorption spectra (DRS) of the CaCO₃–TiO₂ composite photocatalyst as well as the raw materials of CaCO₃ and TiO₂. It can be seen that CaCO₃–TiO₂ and TiO₂ exhibit similar light absorption characteristics. They show no light absorption in the visible light region (wavelengths of 400–800 nm) and show strong absorption in ultraviolet light (wavelengths of 200–400 nm), which is consistent with the bandgap characteristics of the TiO₂ semiconductor (3.2 eV of bandgap width). By contrast, CaCO₃ shows almost no absorption of both visible light and ultraviolet light. The results show that CaCO₃–TiO₂ has similar properties to TiO₂, consistent with the observed strong photocatalytic degradation performance of CaCO₃–TiO₂ and TiO₂ is formed in the creation of CaCO₃–TiO₂.



Figure 5. UV-VIS absorption spectra of CaCO₃, TiO₂ and CaCO₃-TiO₂.

3.3. Morphology and Structure of CaCO₃–TiO₂ Composite Photocatalyst

3.3.1. SEM Analysis

Figure 6 shows SEM images of CaCO₃, nano-TiO₂ raw materials, CaCO₃-TiO₂ composite photocatalyst with different mass ratios of TiO_2 and the physical mixtures of CaCO₃ and TiO₂ (40%) TiO_2 mass ratio). Figure 6a shows that the CaCO₃ particles have a bulk shape with a particle size of about 1–3 μ m, as well as smooth surfaces without coatings. Figure 6b,c shows that the nano-TiO₂ particles are fine, but their agglomeration is severe, with an aggregate size of up to 2 μ m. Figure 6d–g show that when $CaCO_3$ is combined with nano-TiO₂, the surface of $CaCO_3$ particles is uniformly covered by fine particles, and the surface becomes rough. Figure 6i, j are the mapping results of Ca and Ti elements corresponding to Figure 6f; it can be seen that Ca distributes in the particle contour range of CaCO₃, reflecting the characteristic of CaCO₃. The distribution of Ti in the scanning area is uniform, which corresponds to the location of the particles. This proves that the TiO_2 is distributed on the surface of CaCO₃ uniformly. Obviously, the CaCO₃–TiO₂ composite photocatalyst is composed of composite particles characterized by nano-TiO₂ loaded on the CaCO₃ surface. Therefore, it is inferred that CaCO₃-TiO₂ should exhibit the properties of nano-TiO₂ (photocatalytic properties). In addition, it was found that the dispersion of TiO₂ loaded on the surface of CaCO₃ was significantly higher than that of TiO₂ alone. The particle unit size is generally reduced to less than $0.2 \,\mu m$, which allows the active sites of TiO_2 to be more exposed, thereby increasing its photocatalytic performance. This is undoubtedly the intrinsic mechanism enabling CaCO₃-TiO₂ to exhibit a photocatalytic degradation performance comparable to that of pure TiO_2 when the mass ratio of TiO_2 is only 40%.

Figure 6d–f shows that as the mass ratio of TiO_2 increased from 20% to 50%, the surface of the CaCO₃ was coated by nano-TiO₂ particles more and more uniformly and completely. Especially when the mass ratio of TiO₂ was 40%, the surface of CaCO₃ was almost completely covered by TiO₂ particles. However, in the physical mixture of CaCO₃ and TiO₂ with the same composite proportion (Figure 6h), the loading of nano-TiO₂ was very poor. Only a small part of the surface of CaCO₃ particles contained loadings, and most of them were bare. The above results indicate that the co-grinding of CaCO₃ and TiO₂ greatly promotes the loading function, thereby improving the performance of CaCO₃–TiO₂.



Figure 6. SEM images of CaCO₃ (**a**), TiO₂ (**b**,**c**), CaCO₃–TiO₂ composite photocatalyst with TiO₂ mass ratios of 20% (**d**), 40% (**e**), 50% (**f**,**g**). The mixture of CaCO₃ and TiO₂ (**h**). The mapping of Ca (**i**) and Ti (**j**) corresponding to (**f**).

3.3.2. XRD Analysis

Figure 7 displays the XRD spectra of CaCO₃, nano-TiO₂ raw material, CaCO₃–TiO₂ composite photocatalyst and the physical mixture of CaCO₃ and TiO₂. The results reveal that only the characteristic diffraction peaks of calcite appeared in the XRD spectrum of CaCO₃, indicating its high purity. The characteristic diffraction peaks of rutile and anatase appeared in the spectrum of nano-TiO₂, indicating that it consisted of rutile and anatase mixed phase, consistent with the phase composition of P₂₅. In the spectrum of the CaCO₃–TiO₂ composite photocatalyst, only calcite, rutile and anatase crystal phases were observed, indicating that the compounding of CaCO₃ and TiO₂ does not produce a new phase. It was concluded that the combination of CaCO₃ and TiO₂ occurs in their interface region, and the binding properties should be chemical or physical action within the interface area. The phase composite photocatalyst, but the intensity of the characteristic peaks of CaCO₃ in CaCO₃–TiO₂ composite photocatalyst was weaker than that in the physical mixture. This may be due to the reduction of CaCO₃ exposure in CaCO₃–TiO₂ due to the coating of the surface with titanium dioxide, while most of the surface of CaCO₃ in the physical mixture was still bare [23]. The above results also indicate the successful compounding of CaCO₃ and TiO₂ in CaCO₃–TiO₂.



Figure 7. X-ray diffraction (XRD) spectra of CaCO₃, TiO₂, CaCO₃–TiO₂ composite and the physical mixture of CaCO₃ and TiO₂.

3.3.3. Infrared Spectrum Analysis

The infrared spectra of CaCO₃, nano-TiO₂ raw material and CaCO₃–TiO₂ composite photocatalyst were measured, as shown in Figure 8. In the infrared spectrum of nano-TiO₂, the wide absorption band in the range of $3250-3700 \text{ cm}^{-1}$ and the absorption peak at 1636 cm^{-1} respectively represent the stretching vibration and bending vibration of the O–H bond in the water molecules and hydroxyl groups on the surface of TiO₂. The absorption band in the range of about $3300-3500 \text{ cm}^{-1}$ in the CaCO₃ spectrum represents the characteristics of adsorption water and hydroxyl groups on its surface. In the infrared spectrum of the CaCO₃–TiO₂ composite photocatalyst, the absorption peak at 1636 cm^{-1} of TiO₂ disappeared, and the absorption peak of CaCO₃ ranging from $3300 \text{ to } 3500 \text{ cm}^{-1}$ was weakened. It has been suggested that CaCO₃ and TiO₂ form a firm chemical combination through their surface hydroxyl groups [24].



Figure 8. FT-IR spectra of CaCO₃, TiO₂ and CaCO₃-TiO₂ composite.

Based on the above study, the mechanism of $CaCO_3$ as a carrier to improve the photocatalytic performance and utilization efficiency of nano-TiO₂ can be summarized as follows: (1) The dispersibility of TiO₂ is improved by uniformly loading TiO₂ on the surface of CaCO₃, thereby causing an increase in active sites and light absorption areas. (2) A chemical bond is formed between TiO₂ and CaCO₃ at their interface, which provides a new transport channel for the photo electrons [25,26], and further improves the separation efficiency of electrons and holes. (3) In CaCO₃–TiO₂, nano-TiO₂ and CaCO₃ are firmly combined due to their surface chemical bonding, which prevents the loss of TiO₂ when

degrading pollutants in water [9,27]. Therefore, this composite photocatalyst can be easily recovered and recycled from water by sedimentation, thereby reducing the use amount of TiO_2 as well as the cost. Figure 9 is a schematic diagram reflecting the above principles.



Figure 9. Improvement mechanism of photocatalytic performance.

4. Conclusions

- (1) The CaCO₃–TiO₂ composite photocatalyst was prepared by the co-grinding of CaCO₃ and TiO₂. The optimal CaCO₃–TiO₂ composite photocatalyst, in which the particles size of CaCO₃ is 15 µm and the mass ratio of TiO₂ is 40%, shows excellent photocatalytic degradation performance towards methyl orange and good recovery performance. The degradation efficiency of optimal CaCO₃–TiO₂ composite photocatalyst was found to be 90% and 100% after 20 and 40 min of ultraviolet light illumination, respectively. The degradation effect is comparable to pure TiO₂. Moreover, its degradation effect on methyl orange is not significantly reduced after five cycles.
- (2) CaCO₃-TiO₂ composite photocatalyst is characterized by CaCO₃ loaded by nano-TiO₂ uniformly and completely. The dispersibility of the loaded TiO₂ is significantly enhanced compared to pure TiO₂, and a strong chemical bond is formed between CaCO₃ and TiO₂ particle interfaces. These are important mechanisms for improving the photocatalytic efficiency of nano-TiO₂ and reducing the its amount in CaCO₃-TiO₂.

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