Preparation of CaCO\textsubscript{3}-TiO\textsubscript{2} Composite Particles and Their Pigment Properties

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Abstract: CaCO\textsubscript{3}-TiO\textsubscript{2} composite particles were prepared with calcium carbonate (CaCO\textsubscript{3}) and TiO\textsubscript{2} in stirred mill according the wet grinding method. The pigment properties, morphology, and structure of CaCO\textsubscript{3}-TiO\textsubscript{2} composite particles and the interaction behaviors between CaCO\textsubscript{3} and TiO\textsubscript{2} particles were explored. In the CaCO\textsubscript{3}-TiO\textsubscript{2} composite particles, TiO\textsubscript{2} is uniformly coated on the surface of CaCO\textsubscript{3} and the firm combination between CaCO\textsubscript{3} and TiO\textsubscript{2} particles is induced by the dehydration reaction of surface hydroxyl groups. CaCO\textsubscript{3}-TiO\textsubscript{2} composite particles have similar pigment properties to pure TiO\textsubscript{2}. The hiding power, oil absorption, whiteness and ultraviolet light absorption of composite particles are close to those of pure TiO\textsubscript{2}. The application performance of CaCO\textsubscript{3}-TiO\textsubscript{2} composite particles in the paint is consonant with their pigment properties. The contrast ratio of the exterior paint containing CaCO\textsubscript{3}-TiO\textsubscript{2} composite particles is equivalent to that of the paint containing the same proportion of pure TiO\textsubscript{2}.

Keywords: CaCO\textsubscript{3}-TiO\textsubscript{2}; composite particle; pigment; wet grinding

1. Introduction

CaCO\textsubscript{3} is an important inorganic mineral material. Especially, the CaCO\textsubscript{3} powder material prepared with various non-metallic minerals, such as aragonite, calcite, and some rocks with calcite as the main ingredient component, has many advantages, such as high purity, high whiteness, good compatibility with organic and inorganic matrices, and low cost [1,2]. Therefore, CaCO\textsubscript{3} has become the most widely used filler in many industrial products such as plastic, paint, and paper due to its obvious cost advantage compared to most non-metallic minerals [3,4]. In order to further increase the utilization value of CaCO\textsubscript{3} and achieve the efficient utilization of mineral resources, it is necessary to develop CaCO\textsubscript{3}-based composite with oxides, such as TiO\textsubscript{2} [5,6]. Recently, the composite pigment prepared by coating TiO\textsubscript{2} particles on the surface of CaCO\textsubscript{3} particles, had received wide attention [7]. The composite pigment can not only increase the utilization efficiency of pigment TiO\textsubscript{2}, but also reduce the consumption of pigment TiO\textsubscript{2}. The preparation of the composite pigment will enhance the comprehensive utilization of titanium resource [8–10].

TiO\textsubscript{2}-coated mineral materials are generally prepared by hydrolysis precipitation coating method [11,12]. Zhou [13] prepared the TiO\textsubscript{2}-coated barite composite pigments through the hydrolysis of TiOSO\textsubscript{4} on the barite surface. Ninness [14] and Lu [15] prepared TiO\textsubscript{2}-coated kaolin composite pigments and Gao prepared the anatase and rutile TiO\textsubscript{2}-coated mica composite pigments through the hydrolysis coating of TiCl\textsubscript{4} [16,17]. However, a strong acid is produced during the hydrolysis process of titanium salts. CaCO\textsubscript{3} is instable in acid media due to its poor acid fastness. Consequently, the CaCO\textsubscript{3}-based composite could not be prepared through the hydrolysis of titanium salts such as TiOSO\textsubscript{4}.

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Hence, several methods were developed to prepare CaCO$_3$-TiO$_2$ composites. Tanabe [18] prepared CaCO$_3$-TiO$_2$ composite particles through carbonation in the TiO$_2$ system. Liu [19] and Sun [20] prepared CaCO$_3$-TiO$_2$ composite particles by the sol-gel method and hydrophobic agglomeration method, respectively. However, the above mentioned methods are complicated and expensive, and can hardly realize large-scaled industrial production of CaCO$_3$-TiO$_2$ composite particles.

The mechanochemical method is widely used to prepare composite materials due to its simple process, low cost, and low pollution. Through the ultra-fine grinding of mineral particles, the surface of mineral particles can be activated, thus slightly changing the crystal structure and physicochemical properties of the surface. Consequently, the interfacial reaction between particles is strengthened to induce the combination. Wang [21] and Chen [22] respectively prepared barite/TiO$_2$ and TiO$_2$-coated wollastonite composite pigments by the mechanochemical method, and both composite pigments exhibited similar pigment properties to TiO$_2$. However, the combination between barite and TiO$_2$ was induced by electrostatic interactions. Therefore, the combination effect was not firm enough and needs to be enhanced. The light adsorption property or the application performance of the composite pigments was not explored. In this study, CaCO$_3$-TiO$_2$ composite particles were prepared in the water system according to the mechanochemical method. In addition, the pigment properties, light absorption properties, morphology, and structure of the prepared CaCO$_3$-TiO$_2$ composite particles were studied and the combination feature and mechanism between TiO$_2$ and CaCO$_3$ particles were also investigated. Additionally, the application performances of CaCO$_3$-TiO$_2$ composite particles in paint were evaluated.

2. Methods

2.1. Raw Materials

CaCO$_3$ raw material used as the substrate in this study was produced in Huadian Quanxing Mining Co., Ltd. Manufacturer, Huadian, Jilin Province, China. The purity, hiding power, whiteness, and average particle size of the raw material are respectively 100% (indicated by X-ray diffractometer), 185 g/m$^2$, 97.82%, 1.21 µm (d$_{50}$), and 4.87 µm (d$_{90}$), indicating that the CaCO$_3$ raw material has the poor hiding property and high whiteness. The TiO$_2$ raw material used in the experiment is commercially available rutile TiO$_2$ produced by sulfuric acid method (Billionschem Co., Ltd., Jiaozuo, China). The whiteness, hiding powder, oil absorption and average particle size of TiO$_2$ are respectively 96.9%, 14.61 g/m$^2$, 26.06 g/100 g, 0.37 µm (d$_{50}$) and 0.55 µm (d$_{90}$), indicating the excellent pigment properties of TiO$_2$ raw material. Chemically pure linseed oil (Zhengzhou Tianma Art Paints Co., Ltd., Zhengzhou, China) and distilled water were also used (Beijing Jinxin Hengda Technology and Trade Co., Ltd., Beijing, China).

2.2. Preparation

2.2.1. Preparation of the CaCO$_3$-TiO$_2$ Composite Particles

CaCO$_3$-TiO$_2$ composite particles were prepared with CaCO$_3$ and TiO$_2$ in stirred mill by wet grinding. Firstly, the CaCO$_3$ slurry and TiO$_2$ slurry were prepared. CaCO$_3$ and TiO$_2$ were respectively mixed with water and sodium polyacrylate (dispersant) according to a certain proportion and stirred by a high-speed dispersion machine. Secondly, the CaCO$_3$ and TiO$_2$ slurries were mixed together and ground by a GSDM-S3 type ultrafine grinding mill (3 L, Beijing gosdel power&technology Co. Ltd., Beijing, China) with a speed of 1200 r/min and the weight ratio of ball to powder was 4:1. After stirring at room temperature and pH = 8 for 90 min, the composite slurry was obtained. Finally, the CaCO$_3$-TiO$_2$ composite particles were obtained after the CaCO$_3$-TiO$_2$ composite slurry was dried at 100 °C for 12 h (Electric thermostaticdrying oven, Tianjin Taisite Instrument Co., LTD, Tianjin, China).
2.2.2. Preparation of the Construction Paint for Exterior Wall

The construction paints for exterior wall was prepared respectively with CaCO$_3$-TiO$_2$ composite particles and TiO$_2$ particles as pigments. The raw materials were added into a high-speed mixer sequentially according to a certain proportion and then stirred to form a stable paint. In the paint, the TiO$_2$ or the CaCO$_3$-TiO$_2$ composite particles were used as white pigment, they impart opacity to the coating by bonding with the film-forming materials. The ground calcium carbonate was used as the main filler, playing a role in filling and reducing the cost of coatings. The total content of white pigment and ground calcium carbonate was 35.5 wt %. Besides, the acrylic emulsion was used as a film former, which allows the coating to be firmly adhered to the substrate to form a continuous film. Several additives including wetting agent, water, dispersant, pH regulator, defoamer, film-forming additive, leveling agent, and thickener were added to adjust the coating performance.

2.3. Characterization

2.3.1. Structure and Property Characterization

We observed the morphology of CaCO$_3$, TiO$_2$, and CaCO$_3$-TiO$_2$ composite particles by scanning electron microscope (SEM, S-3500N, HITACHI, Tokyo, Japan) under an energy dispersive spectrocope at 5.0 kV and transmission electron microscope (TEM, FEI Tecnai G2 F20, Portland, OR, USA) under an acceleration voltage of 300 kV. For morphological observation, the powder samples were dispersed in ethanol solvent and sonicated for 10 min, and then the suspensions were directly dropped to the conductive adhesive or copper net for natural drying. The phase analysis were carried out on the X-ray diffractometer (XRD, D8 ADVANCE, BrukerAXS GmbH, Karlsruhe, Germany) with Cu Kα radiation ($\lambda = 1.5406$ Å) generated at 40 kV and 15 mA and a scanning rate of 8°/min. The Fourier-transform infrared (FT-IR) spectra were recorded on an infrared spectrooscope (Spectrum 100, PerkinElmer Instruments (Shanghai) Co., Ltd., Shanghai, China) in a scanning range of 4000–400 cm$^{-1}$. The particle size was tested with centrifugal sedimentation (BT-1500, Dandong Bettersize Instrument (Liaoning) Co., Ltd., Liaoning, China). The whiteness was tested with a whiteness meter (SBDY-1, Shanghai Yuet Feng Instrument Co., Ltd., Shanghai, China). The ultraviolet (UV)-vis spectra of the prepared composite materials were obtained in the range of 200–800 nm on a TU-1901 double beam spectrophotometer (Beijing Presec General Instrument Co., Ltd. Beijing, China).

2.3.2. Property Tests of the CaCO$_3$-TiO$_2$ Composite Particles and the as-Prepared Paint

The pigment properties of the CaCO$_3$-TiO$_2$ composite particles were evaluated in terms of oil absorption, hiding power, and relative hiding power and the previous testing methods [23,24] were adopted.

Oil absorption is an important index of pigments. According to the China National Standard GB/T 5211.15-2014 [25], the index refers to the minimum amount of varnish (linseed oil) required for completely wetting 100 g pigment.

Hiding power is another important index of pigments. It refers to the minimum amount of pigment required for completely covering a black and white checkerboard. The hiding power of a pigment can be tested according to the China National Industrial Standard HG/T 3851-2006 [26] (the Test Method of Pigment Hiding Power).

The relative hiding power (R, %) is defined as the ratio of the hiding power of the composite particles to that of pure TiO$_2$ pigment. The R value can be calculated as:

$$ R = \left( \frac{H_T}{H_{CT}} \right) \times 100\% , $$

where $H_T$ (g/m$^2$) and $H_{CT}$ (g/m$^2$) are respectively the hiding power values of TiO$_2$ and the CaCO$_3$-TiO$_2$ composite particles.
The value of $\Delta R$ calculated by Equation (2) represents the increase in the hiding power of TiO$_2$ caused by the combination with CaCO$_3$:

$$\Delta R = R - R_0$$  \hspace{1cm} (2)$$

where $R_0$ is the mass ratio of TiO$_2$ to the composite particles.

According to the China National Standard GB/T 23981-2009 [27], the contrast ratio of the construction paint for exterior wall (C) can be tested according to the following method. A coating film with a certain thickness was firstly coated on the standard black-and-white plate and then the reflectivity values of black ($R_B, \%$) and white regions ($R_W, \%$) were tested with a reflectivity measuring instrument (C84-III, Tianjing Jinke Material Testing machine Co., Ltd., Tianjing, China). Finally, the contrast ratio of coating film can be obtained by Equation (3) [23]:

$$C = \frac{R_B}{R_W}$$  \hspace{1cm} (3)$$

The total color difference ($\Delta E$) between the paint containing CaCO$_3$-TiO$_2$ composite particles and the paint containing TiO$_2$ pigment can be calculated by Equation (4):

$$\Delta E = [(L_T^* - L_{CT}^*)^2 + (a_T^* - a_{CT}^*)^2 + (b_T^* - b_{CT}^*)^2]^{1/2}$$  \hspace{1cm} (4)$$

where the $L_T^*$, $a_T^*$, and $b_T^*$ represent the chromaticity values of coating films containing TiO$_2$ particles; $L_{CT}^*$, $a_{CT}^*$, and $b_{CT}^*$ represent the chromaticity value of coating films containing CaCO$_3$-TiO$_2$ composite particles. All the chromaticity values were measured with a portable integrating sphere spectrophotometer (X-Rite Sp60, X-Rite (Shanghai) International Trade Co., Ltd., Shanghai, China).

3. Results and Discussion

3.1. Morphology of CaCO$_3$-TiO$_2$ Composite Particles

The uniformity and completeness of TiO$_2$ coating on the surfaces of minerals are important influencing factors of the pigment properties of minerals-TiO$_2$ composite particles. Therefore, we investigated the morphology of CaCO$_3$ and TiO$_2$ raw materials, as well as CaCO$_3$-TiO$_2$ composite particles with different mass ratios of TiO$_2$. Corresponding SEM and TEM images are shown in Figure 1.

![Figure 1](image-url)
In Figure 1a, the bulk CaCO3 particles with the size of 1–3 μm were obvious and the surfaces of CaCO3 particles were smooth, without covering. In Figure 1b, the granular TiO2 particles with the particle size of 0.2–0.3 μm showed good dispersivity. However, after CaCO3 and TiO2 particles were ground together (Figure 1c–e), many fine particles were uniformly coated on the surfaces of CaCO3, and the smooth surface of CaCO3 became rough. As indicated by the Energy Dispersive Spectrometer (EDS) results (Figure 1d), the particles coated on the surfaces of CaCO3 should be TiO2. Apparently, the CaCO3-TiO2 composite particles were characterized by the uniform TiO2 coating on the surface of CaCO3. Consequently, the CaCO3-TiO2 composite particles should possess the properties of TiO2, such as the similar pigment properties to that of TiO2.

The uniformity and completeness of the TiO2 coating on the surfaces of CaCO3 particles increased accordingly when the mass ratio of TiO2 increased from 30% to 50% (Figure 1c–e). Particularly, when the mass ratio of TiO2 increased to 50%, the surfaces of the CaCO3 particles were almost completely covered by TiO2 particles. Additionally, as shown in the TEM image (Figure 1f), the CaCO3-TiO2 composite particles are composed of the particles characterized by uniform and dense TiO2 coating on the surface of CaCO3.

3.2. Binding Properties of CaCO3 and TiO2 Particles

3.2.1. XRD Analysis

Figure 2 shows the XRD pattern of CaCO3, TiO2, and CaCO3-TiO2 composite particles with the TiO2 mass ratio of 50%. There were only calcite and rutile diffraction peaks in the XRD pattern of CaCO3-TiO2 composite particles, indicating that the composite particles were still composed of calcite and rutile TiO2, and no new phase was produced in the preparation process of the composite particles. Meanwhile, the complete crystal phases of the CaCO3 and TiO2 materials remained without any changes. Therefore, it can be inferred that the binding of CaCO3 and TiO2 particles should occur at the interfacial region of the particles, whether the binding is of a chemical or physical nature.

![Figure 2](image-url)  
*Figure 2. X-ray diffractometer (XRD) patterns of CaCO3, TiO2, and CaCO3-TiO2 composite particles.*

3.2.2. Infrared Spectral Analysis

In addition to the coating behaviors of TiO2, including completeness and orderliness, on the surfaces of mineral particles, the binding properties and binding strength between mineral particles and TiO2 particles are also important influencing factors of the properties of the TiO2-coated composite particle pigments. In order to investigate the binding properties between TiO2 and CaCO3 particles,
the infra-red (IR) spectra of TiO₂, CaCO₃, and CaCO₃-TiO₂ composite particles were tested and analyzed (Figure 3). Figure 3a displays several peaks in the range of 400–700 cm⁻¹, which are ascribed to the stretching vibrations of Ti-O-Ti bonds. These peaks were characteristic peaks of TiO₂ [28,29]. In Figure 3b, the absorption peaks at 880 cm⁻¹ and 718 cm⁻¹ were ascribed to the characteristic absorption peaks of CO₃²⁻ in CaCO₃ [30,31]. Meanwhile, the peak at 3420 cm⁻¹ was ascribed to the hydroxyl groups formed by the reaction between H₂O and the ions on CaCO₃ surface such as Ca²⁺ and CO₃²⁻. Several changes were observed in the IR spectrum of CaCO₃-TiO₂ composite particles (Figure 3c), compared to that of the raw materials. Firstly, the absorption peak of CO₃²⁻ in CaCO₃ appeared at 1465 cm⁻¹, showing a shift and broadening phenomenon compared with the absorption peak at 1440 cm⁻¹ in the infrared spectrum of CaCO₃. The shifted absorption peak indicated that the chemical environment of CO₃²⁻ changed due to the reaction with other materials, and the broadened absorption peak showed that the association degree between CaCO₃ particles increased. Secondly, compared to the characteristic peak of hydroxyl groups at 3420 cm⁻¹ in CaCO₃ raw materials (Figure 3b), the characteristic peak of water and hydroxyl groups at 2892–3300 cm⁻¹ in Figure 3c [32] was broadened and shifted in the direction of the low wave number. Thirdly, there is a clear absorption peak at 1030 cm⁻¹ in Figure 3c, indicating that there might be a chemical bonding behavior related to the formation of Ti-O-Ca bond. According to the above analysis, it can be inferred that the combination of CaCO₃ and TiO₂ should be realized by the chemical interaction between hydroxyl groups on particle surfaces, so this combination should be firm. Undoubtedly, based on the uniform coating of TiO₂ on the surface of CaCO₃, the strong combination strength between CaCO₃ and TiO₂ largely determines the good pigment properties of CaCO₃-TiO₂ composite particles.

![Figure 3. Fourier-transform infrared spectra (FT-IR) spectra of (a) CaCO₃, (b) TiO₂, and (c) CaCO₃-TiO₂ composite particles.](image)

3.2.3. Mechanism Analysis

The hydration behavior of unsaturated ions on the cleavage planes of CaCO₃ and TiO₂ can explain the formation of surface hydroxyl groups. The calcite CaCO₃, which belongs to the tripartite crystal system, is completely cleaved on the plane (10̅1̅1), and the unsaturated Ca²⁺ and CO₃²⁻ ions are exposed. The unsaturated Ca²⁺ on CaCO₃ surface will undergo the following hydration reactions:

\[
\text{Ca}^{2+} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}^+ + \text{H}^+ \quad (5)
\]

\[
\text{Ca(OH)}^+ + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + \text{H}^+ \quad (6)
\]
The above hydration reactions of Ca\(^{2+}\) are related to the pH value. The larger the pH value is, the stronger the hydration effect is \([33,34]\). Therefore, the hydration reaction of CaCO\(_3\) is intense. Obviously, there should be a certain amount of hydroxyl groups on the surfaces of CaCO\(_3\) generated in the hydration reactions of Ca\(^{2+}\) and CO\(_3^{2-}\). As for TiO\(_2\), the hydration reactions of Ti\(^{4+}\) are intense. Hydrolysis reactions and corresponding constants \([35]\) are provided as follows:

\[
\begin{align*}
\text{Ti}^{4+} + H_2O & \rightleftharpoons \text{Ti(OH)}^{3+} + H^+, \text{pk}_1 = 14.15 \\
\text{Ti(OH)}^{3+} + H_2O & \rightleftharpoons \text{Ti(OH)}_2^{2+} + H^+, \text{pk}_2 = 13.73 \\
\text{Ti(OH)}_2^{2+} + H_2O & \rightleftharpoons \text{Ti(OH)}_3^{+} + H^+, \text{pk}_3 = 13.39 \\
\text{Ti(OH)}_3^{+} + H_2O & \rightleftharpoons \text{Ti(OH)}_4 + H^+, \text{pk}_4 = 13.06
\end{align*}
\]

Therefore, a large amount of hydroxyl groups are formed on the TiO\(_2\) surface due to the intense hydrolysis of Ti\(^{4+}\). Consequently, it can be inferred that CaCO\(_3\) and TiO\(_2\) are combined together by the reaction of hydroxyl groups on their surfaces.

Based on the above analysis, the preparation mechanism of CaCO\(_3\)-TiO\(_2\) composite particles by the mechanochemical method can be summarized as follows (Figure 4). First, through the high speed stirring of raw materials, the CaCO\(_3\) and TiO\(_2\) particles can be further dispersed, and then the hydration, dehydration, and other reactions between particles in aqueous media can be promoted because the slight distortion of the lattice of mineral particles and the activation of the particle surface during the grinding process enhances the binding between the surfaces \([36]\). Second, the high energy imported in the co-grinding process can increase the chance of the collision between CaCO\(_3\) and TiO\(_2\) particles, overcome the energy barrier of the repulsive interaction between the two particles, and reduce the distance between particles below the range allowing the interaction between functional groups on particle surface. Finally, the firm combination of CaCO\(_3\) and TiO\(_2\) particles can be achieved by the dehydration reaction among the hydroxyl groups on particle surface.

![Figure 4. Preparation mechanism of CaCO\(_3\)-TiO\(_2\) composite particles.](image)

3.3. Properties of CaCO\(_3\)-TiO\(_2\) Composite Particles

3.3.1. Pigment Properties

Figure 5 shows the pigment properties of CaCO\(_3\), TiO\(_2\) raw materials, and the CaCO\(_3\)-TiO\(_2\) composite materials with different TiO\(_2\) mass ratios, including hiding power, relative hiding power (R), the increased ratio of hiding power (ΔR), oil absorption, and whiteness.

As shown in Figure 5a, CaCO\(_3\)-TiO\(_2\) composite particles exhibited much better hiding properties than CaCO\(_3\). When the mass ratio of TiO\(_2\) in the CaCO\(_3\)-TiO\(_2\) composite was only 30%, its hiding
power reached about 23 g/m², which shows much stronger hiding properties than the CaCO₃ raw material (185 g/m²). When the mass ratio of TiO₂ increases to 50%, the hiding power and relative hiding power of CaCO₃-TiO₂ composite are 17.59 g/m² and 82.80% (R), which was 32.80% (ΔR) higher than that of TiO₂ (R₀). As expected, the hiding power and relative hiding power of the CaCO₃-TiO₂ composite respectively reached 15.79 g/m² and 92.27% when the TiO₂ mass ratio increased to 70%, indicating that the CaCO₃-TiO₂ composite have obtained the excellent pigment properties equivalent to that of TiO₂ pigment. Obviously, the coating of TiO₂ on the surface CaCO₃ weakened the properties of CaCO₃ and induced the composite particles to exhibit the properties of TiO₂. The abovementioned results indicated that the TiO₂ particles in the CaCO₃-TiO₂ composite exhibited the higher utilization efficiency compared to the pure rutile TiO₂ pigment because the coating structure improved the dispersion of titanium dioxide and the synergistic effect of calcium carbonate as a carrier. Meanwhile, the whiteness of CaCO₃-TiO₂ composite particles was also close to that of CaCO₃ and TiO₂, and the oil absorption of CaCO₃-TiO₂ composite was similar or less than that of TiO₂.

3.3.2. Optical Property of CaCO₃-TiO₂ Composite Particles

The UV-vis absorption spectra of CaCO₃-TiO₂ composite particles, CaCO₃ and TiO₂ raw materials are shown in Figure 6. All samples almost showed no absorption of visible light in the wavelength range of 400–800 nm, reflecting their characteristics as white inorganic material. However, the three samples are different in the absorption of ultraviolet light in the wavelength range of 200–400 nm. CaCO₃ raw materials exhibited almost no light absorption, but TiO₂ and CaCO₃-TiO₂ composite particles exhibited strong light absorption. CaCO₃-TiO₂ composite particles exhibited less light absorption in the wavelength range of 200–350 nm than TiO₂. Unlike CaCO₃, the CaCO₃-TiO₂ composite particles obtained the same light absorption property as that of TiO₂ and the result was in agreement with the previous report [5]. The abovementioned results not only indicated that the CaCO₃-TiO₂ composite particles obtained excellent UV resistance stability, but also reflected the mechanism that TiO₂ particles coated on the surface of CaCO₃ particles endowed the composite particles with the similar properties of TiO₂.

Figure 5. Pigment properties of CaCO₃-TiO₂ composite particles with different mass ratios of TiO₂. (a) Hiding power (R) and relative hiding power (ΔR), (b) Oil absorption and whiteness.

Figure 6. UV-vis absorption spectra of CaCO₃, TiO₂, and CaCO₃-TiO₂ composite particles.
3.3.3. Properties of the Exterior Paint Containing CaCO$_3$-TiO$_2$ Composite Particles

Figure 7 shows the property of the exterior paint containing CaCO$_3$-TiO$_2$ composite particles (R-801, the mass ratio of TiO$_2$ is 70%) and rutile TiO$_2$ (BLR-699). As shown in Figure 7a, when the addition proportions of R-801 and BLR-699 in the paint were only 5%, the contrast ratios of the obtained paints respectively reached 0.94 and 0.95, and the two values were close. Moreover, the abovementioned contrast ratios of the paint were higher than the contrast ratio (0.93) of superior products required in China National Standard of Exterior Paints (GB/T 9756-2009) [37], indicating that R-801 and BLR-699 exhibited excellent pigment properties when they were applied in the paint.

When the addition proportions of R-801 and BLR-699 in the paint increased to 10% or more, the contrast ratio of the paint was increased slightly. The contrast ratio of the paint containing R-801 was always equivalent to that of the paint containing BLR-699, indicating that the application of CaCO$_3$-TiO$_2$ composite particles as the pigment in the paint for exterior wall could achieve the equivalent covering effect to the paint containing the same proportion of TiO$_2$. When the addition proportion of pigments in the paint is 5% or 10%, the whiteness of the paint containing R-801 was always lower than that of the paint containing the same proportion of BLR-699 (Figure 7b). However, when the addition proportion of pigments increased to 15% and 20%, the whiteness of the paint containing R-801 was close to that of the paint containing BLR-699 and the color difference value ($\Delta E$) was reduced to about 0.7. As the addition proportion of pigment in the paint for exterior wall is generally high, the comprehensive performance of the paint containing R-801 is equivalent to that of the paint containing BLR-699. As shown in the SEM images of the dry paints respectively containing R-801 and BLR-699 (Figure 8), the two samples all present a continuous form composed of solid particles, such as the polymer formed after emulsion evaporation, binder, pigments, and fillers, indicating that both the R-801 and BLR-699 have good compatibility with emulsion.

![Figure 7](image1.png)

**Figure 7.** Properties of the two exterior paints respectively containing R-801 and BLR-699. (a) Contrast ratio of paint; (b) Whiteness and chromatic aberration of paint.

![Figure 8](image2.png)

**Figure 8.** SEM images of two exterior paints respectively containing R-801 (a) and BLR-699 (b).
4. Conclusions

CaCO$_3$-TiO$_2$ composite particles were prepared with CaCO$_3$ and TiO$_2$ in stirred mill according to the wet grinding method. The composite particles are characterized by the uniform TiO$_2$ coating on the surface of CaCO$_3$. The CaCO$_3$ and TiO$_2$ particles were firmly combined together through the dehydration reaction of hydroxyl groups on their surfaces.

CaCO$_3$-TiO$_2$ composite particles exhibited similar pigment properties and light absorption property to TiO$_2$. Moreover, the CaCO$_3$-TiO$_2$ composite particles also showed excellent application performance. The contrast ratio of the exterior construction paint containing CaCO$_3$-TiO$_2$ composite particles as the pigment was similar to that of paint containing the same proportion of TiO$_2$, and was higher than the contrast ratio (0.93) of superior products required in the China National Standard of Exterior Paints (GB/T 9756-2009 [36]).

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