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Preparation of TiO₂-coated barite composite pigments by the hydrophobic aggregation method and their structure and properties

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We obtained hydrophobic barite (BaSO₄) and rutile titanium dioxide (TiO₂) particles (as raw materials) by organic surface modification. Subsequently, TiO₂-coated barite composite pigments were prepared via the hydrophobic aggregation of heterogeneous particles in a water medium. The pigment properties of the TiO₂-coated barite composite pigments were characterized and evaluated by determining their hiding power, oil absorption value and whiteness. The optical properties were determined by obtaining their UV-vis diffuse reflectance spectra and using the CIE-L*a*b* method. The morphology and bonding properties were investigated using scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and infrared spectroscopy (IR). The results show the similarity between the composite pigment and pure rutile TiO₂: when the mass ratio of rutile TiO₂ in the composite pigment was 60%, the hiding power of the TiO₂-coated barite composite pigment was 90.81% of that of pure rutile TiO₂. Moreover, the surfaces of the barite particles were uniformly and firmly coated by TiO₂, with a hydrophobic association occurring between the hydrophobic carbon chains on the surfaces of barite and TiO₂ particles.

As a transition metal oxide with excellent properties, TiO₂ has demonstrated utility in many applications, including solar energy harvesting, photocatalytic hydrogen production^{1,2} and white pigment. A series of TiO₂ species with different morphology, structure and properties have been prepared, such as TiO₂ nanotubes^{3,4} TiO₂ nano-sheets, and TiO₂ microparticles. Among these species, TiO₂ nanotube-based materials have great potential in various applications as photocatalysts^{5,6} and sensors because of their outstanding optical^{7,8} and electrical properties. Additionally, in the pigment field, TiO₂ microparticles have advantages for certain applications because of their appropriate particle size, which locates them within the best range for scattering visible light. Titanium dioxide pigment is a functional powder material consisting of the TiO₂ crystal phase with a particle size of 200–300 nm. The high refractive index of TiO₂ (2.7 of rutile and 2.3 of anatase) endows it with excellent properties, such as a strong hiding power, a high tintorial strength, a high glossiness, and a strong whiteness. Therefore, titanium dioxide has become the best white pigment and is applied in numerous fields, for example, in paints, plastics, paper, inks and rubber products^{9,10}. However, there are several problems with the application of TiO₂, such as particle aggregation and poor compatibility with organic matrices. Because of these hindrances, the pigment properties of TiO₂ are often exerted ineffectively, causing a reduction in its efficiency and an increase in the amount used. Consequently, concerns regarding the environment and increased resource use during the production of TiO₂ have arisen^{11,12}. To improve the dispersion of TiO₂ and the compatibility of TiO₂ with organic matrices, researchers have focused on developing new inorganic pigments comprising inorganic particles uniformly and firmly coated with TiO₂¹³. In these research, many inorganic non-metallic minerals have been used as substrates, including calcined kaolin¹⁴, sericite¹⁵, and silica¹⁶. Methods such as homogeneous hydrolysis¹⁷ and mechanochemistry have also been applied to the preparation of TiO₂-coated inorganic composite particles.

Barite is an inorganic non-metallic mineral with a chemical composition of BaSO₄. Traditionally, the barite industry mainly produces primary products of low-added value, including petroleum, weighting material for

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Figure 1. SEM images of (a) barite raw material and (b) rutile TiO₂ raw material.

drilling mud in natural gas operations, and barium-containing chemical products¹⁸. Recently, a series of studies on new functional barite materials have been conducted to exploit the excellent optical properties, good dispersibility, chemical stability, and anti-radiation properties of fine barite particles and to explore synergistic effects¹⁹. Barite has a strong whiteness, a low oil absorption and a similar density to TiO₂. Therefore, composite pigments with a similar density to TiO₂ can be prepared using barite and TiO₂ as raw materials. In this way, the mixed homogenization of a composite pigment and a matrix material can be improved, resulting in an improvement in production. Zhou²⁰ has prepared barite-TiO₂ composite particles by hydrolysing TiOSO₄ on the surfaces of barite particles. Wang²¹ and Zhou²² have separately used the mechanochemistry method to prepare anatase and rutile TiO₂-coated barite composite pigments with pigment properties are similar to those of TiO₂.

By contrast, to prepare TiO₂-coated barite composite pigments via the hydrolysis of TiOSO₄²⁰ the precipitation product is amorphous TiO₂, which should be calcined at 800–900 °C for conversion to crystalline TiO₂. Inevitably, the calcination consumes a large amount of energy, and converting the TiO₂•nH₂O on the surface of barite into the rutile single-crystal phase is difficult. The mechanochemistry method^{21,22} also consumes considerable energy because the composite pigments are prepared using a grinding mill with high power. Meanwhile, TiO₂-coated barite composite pigments prepared by the two aforementioned methods have a hydrophilic surface, leading to their poor compatibility with organic matrices and a reduction in their usage efficiency. For the above reasons, a hydrophobic aggregation method has been used in this study in order to obtain uniformly and firmly TiO₂-coated barite composite pigments with a hydrophobic surface while consuming less energy.

Hydrophobic aggregation refers to the aggregation of fine particles that attract each other because of their hydrophobic surfaces²³. The attraction occurs at a particle distance ranging from 2 to 25 nm in a water medium, and the attraction strength is 10–100 times stronger than that of the electrical double layer force and Van der Waals force²⁴. In particular, when the hydrophobic surfaces of particles are induced by surface modification, a strong aggregation occurs among the particles because of the association between the hydrocarbon chains on the surfaces. The abovementioned condition results in the particles combining firmly. The hydrophobic aggregation phenomenon of particles was first observed in the mineral flotation process, which has been improved and applied constantly. However, the existing studies mainly focus on the hydrophobic aggregation of homogeneous mineral particles in raw ore. For example, Song^{25,26} has studied the hydrophobic aggregation and separation of fine rutile, haematite and hydrophobic coal particles. Furthermore, research regarding the hydrophobic aggregation and flotation of galena, sphalerite, rhodochrosite and other fine-grained minerals has been reported²⁷. By contrast, there are fewer studies on the hydrophobic aggregation of heterogeneous particles, especially for the preparation of composite pigments through the hydrophobic aggregation of TiO₂ and mineral particles. Because the hydrophobic aggregation of TiO₂ and mineral particles needs to be based on the selective recognition among particles, performing this work is a significant challenge. In this study, TiO₂-coated barite composite pigments were prepared via the hydrophobic aggregation of barite and TiO₂ particles in a water medium. Meanwhile, their morphology, structure, and bonding properties were studied. Their pigment properties were also characterized and evaluated.

Experimental

Materials. The barite raw material used as the substrate in this study was produced in Hubei Province, China, and had a purity of 100%, a whiteness of 89.40%, a hiding power of 155.00 g/m² and an oil absorption of 11.40 g/100 g. Figure 1(a) shows the morphology of the barite raw material, as determined by scanning electron microscope (SEM), wherein the barite particles were well dispersed and exhibited plate- and lump-like shapes. The particles possessed a uniform size distribution.

The rutile TiO₂ raw material was produced in Henan Province, China, and had a whiteness of 94.40%, a hiding power of 10.97 g/m², and an oil absorption of 24.26 g/100 g. Figure 1(b) shows the granular rutile TiO₂ with an average particle size of 300 nm.

Analytical-grade sodium stearate (CH₃(CH₂)₁₆COONa), sulfuric acid (H₂SO₄) and sodium hydroxide (NaOH) were used in the experiments. Meanwhile, we used chemically pure linseed oil and distilled water.

Figure 2. Flowchart of the preparation of the TiO₂-coated barite composite pigments.

Preparation method. The TiO₂-coated barite composite pigments were prepared via the hydrophobic aggregation method, which is illustrated in the flowchart in Fig. 2. The modified TiO₂ slurry (MTS) was obtained through the following way: rutile TiO₂ powder was dispersed in water, mixed with 3% mass ratio modifier (CH₃(CH₂)₁₆COONa) and stirred for approximately 45 min at 60 °C. And for comparison, the unmodified TiO₂ slurry (UTS) was prepared via the same process without the addition of modifier. Similarly, the modified barite slurry (MBS) was prepared: barite powder was dispersed in water, mixed with 1% mass ratio modifier (CH₃(CH₂)₁₆COONa) and stirred for approximate 45 min at 70 °C, and the unmodified barite slurry (UBS) was also prepared via the same way without the addition of modifier. Afterwards, the composite process was conducted: the MBS was mixed with different mass ratios of the MTS. After stirring for 60 min at a pH value of 9, we obtained a barite-TiO₂ slurry. Finally, the barite-TiO₂ slurry was dried at 60 °C, and then the TiO₂-coated barite composite pigments were prepared.

As a comparison, composite particles fabricated using UBS and UTS as raw materials were also prepared (discussed in 3.4.1). For Sample 1, the composite materials were prepared using UBS and UTS as the raw materials, the Sample 2 used MBS and UTS as raw materials, and the Sample 3 used UBS and MTS as raw materials. For all the three samples, the mass ratio of TiO₂ to barite was 6:4, and the composite process was carried out through the way described in the previous paragraph. Subsequently, all the prepared slurries were dried at 60 °C to obtain the composite particles.

Characterization. *Pigment properties.* The pigment properties of the TiO₂-coated barite composite pigments were evaluated by determining the oil absorption value, hiding power, relative hiding power and whiteness. The test methods were as follows.

Oil absorption is an important index of pigment properties, this value refers to the minimum amount of varnish (linseed oil) that can wet 100 g of the pigment completely. The oil absorption of a pigment can be tested basing on the China National Standard GB/T5211.15-2014.

Hiding power is another important and insightful index of pigment properties. It refers to the minimum amount of pigment that can completely cover a black and white checkerboard. The hiding power of a pigment can be tested using the National Industry Standards HG/T3851-2006 (the test method of pigment hiding power).

The relative hiding power (R) indicates the hiding property ratio of the composite pigment to a pure TiO₂ pigment according to the definition of pigment hiding power. The R value can be calculated using Equation (1)

$$R = (H_T/H_{CT}) \times 100\% \quad (1)$$

where H_T (g/m²) and H_{CT} (g/m²) are the hiding powers of TiO₂ and the TiO₂-coated barite composite pigments, respectively.

The value of ΔR calculated by Equation (2) represents the magnitude of the increase in the hiding power of TiO₂ upon forming its composite with barite.

$$\Delta R = R - R_0 \quad (2)$$

where R_0 is the mass ratio of TiO₂ to the composite pigment.

The whiteness was tested using a whiteness meter (SBDY-1, Shanghai Yuet Feng Instrument Co. Ltd., China).

Optical properties. The optical properties of the TiO₂-coated barite composite pigments were characterized by acquiring their UV-vis diffuse reflectance spectra and using the CIE-L*a*b* method. The UV-vis spectra of the prepared composite pigments were obtained between 200 and 800 nm on a TU-1901 double beam

Mass ratio of rutile TiO ₂ (R ₀) /%	Contact angle/°	Oil absorption /(g/100 g)	Whiteness/%	Hiding power/ (g/m ²)	Relative hiding Power (R)/%	ΔR (R-R ₀) /%
0 (barite)	22.50	11.40	89.40	155.00	—	—
20	95.80	12.20	90.12	22.85	48.01	28.01
40	110.20	12.56	90.97	15.18	72.27	32.27
50	112.50	12.85	91.35	13.16	83.36	33.36
60	115.60	14.48	91.80	12.08	90.81	30.81
80	109.40	16.79	92.39	11.15	98.38	18.38
100(TiO ₂)	33.20	24.26	94.40	10.97	100.00	—

Table 1. Pigment properties of the TiO₂-coated barite composite particles.

spectrophotometer. The L*a*b* parameters of representative specimens were measured using a portable integrating sphere spectrophotometer (X-Rite Sp60, X-Rite (Shanghai) International Trade Co., Ltd., China). The CIE-L*a*b* colourimetric method recommended by the CIE (Commission Internationale de l'Éclairage) was followed. In this colour system, L* is the colour lightness (L* = 0 for black and 100 for white), a* is the green (−)/red (+) axis, and b* is the blue (−)/yellow (+) axis²⁸.

Morphology and structure. The hydrophobic properties of the particles were evaluated based on the wet contact angle obtained by contact angle measurement (JC2000D, Shanghai Zhongchen Digital Technic Apparatus Co. Ltd., China). First, the powder samples were pressed into a thin sheet with a smooth surface by a tablet pressing machine. Next, the contact angle of the samples was measured three times. Then, the results were averaged. The images of TiO₂-coated barite particles dispersed in an organic medium were obtained by an image analyser (BT-1600, Bettersize Instruments Ltd., China).

We observed the morphology of barite, rutile TiO₂, and TiO₂-coated barite composite pigments by SEM (S-3500N, HITACHI, Japan). The surface functional groups were examined by infrared spectroscopy (Spectrum 100, PerkinElmer Instruments (Shanghai) Co. Ltd., China) using KBr as the medium. Further analysis was carried out using X-ray photoelectron spectroscopy (XPS, Escalab 250xi, Thermo Fisher Scientific USA) and X-ray diffraction (D/MAX2000, Rigaku Corporation, Japan).

Results and Discussion

Pigment properties of TiO₂-coated barite composite pigments. Barite and rutile TiO₂ particles were modified using sodium stearate. Based on the induced surface hydrophobicity of the modified particles (the wetting contact angles of barite and TiO₂ particles are 128.5° and 114.2°, respectively), TiO₂-coated barite composite pigments with different TiO₂ mass ratios were prepared via the hydrophobic aggregation method. Table 1 shows the pigment properties of the TiO₂-coated barite composite pigments and raw materials.

The results show that the hiding power of the barite raw material is 155.00 g/m², which indicates no hiding properties. However, the hiding power clearly improved after the barite particles were coated by TiO₂ particles and increased as the TiO₂ mass ratio increased. When the TiO₂ mass ratio increased to 60%, the hiding power and relative hiding power (R) of the TiO₂-coated barite composite pigments were 12.08 g/m² and 90.81%, respectively, nearly reaching the levels observed for pure rutile TiO₂, for which the R value exceeds 30.81% (ΔR) compared with the mass ratio of TiO₂ (R₀). In addition, the TiO₂-coated barite composite pigments had a lower oil absorption value than that of TiO₂ and a similar whiteness to TiO₂. Additionally, the contact angle of the composite particles was more than 100°. The above results show that the TiO₂-coated barite composite pigments possessed pigment properties that were completely different from those of barite but similar to those of TiO₂. Furthermore, the composite pigments exhibited hydrophobicity. It can be concluded that the barite particles were uniformly and firmly coated by TiO₂ particles.

Figure 3 shows the morphology of the TiO₂-coated barite composite pigments with different TiO₂ mass ratios. Figure 3a,b and c show that the number of TiO₂ particles and the coated area of the barite surface increased remarkably as the TiO₂ mass ratio increased from 20% to 60%, giving a uniform coating. Particularly, when the TiO₂ mass ratio increased to 60%, the surfaces of the barite particles were nearly completely covered by the TiO₂ particles. The results in Table 2 show the atomic percentages of different samples obtained from XPS analysis. Clearly, as the mass fraction of TiO₂ increases, the percentage of Ti atoms on the surface of the barite particles increased, whereas the number of Ba atoms decreased. Meanwhile, the value of Ti/Ba increased as the TiO₂ mass fraction increased. The above results show that the TiO₂ coated on the barite surface becomes more compact as the TiO₂ content increases. The SEM and XPS results are consistent with the results in Table 1.

Optical properties of TiO₂-coated barite composite particles. There are several methods for measuring the colour of pigments, and the CIE-L*a*b* values were used to specify and compare the colour of the TiO₂-coated barite composite pigments with different TiO₂ mass ratios. Table 3 shows the results.

The L* value of the TiO₂-coated barite composite pigment gradually increased with the TiO₂ mass ratio until it was close to that of rutile TiO₂. This observation indicates that the lightness of the composite pigments improved because of the coating of TiO₂ particles on the barite particles surface. Similarly, the a* and b* values of the TiO₂-coated barite composite particles are also close to those of rutile TiO₂ at increased TiO₂ mass ratios. Meanwhile, the total colour difference (ΔE) between the TiO₂-coated barite composite pigments and rutile TiO₂,

Figure 3. SEM images of the barite-TiO₂ composites with different TiO₂ mass ratios (a) 20%, (b) 40%, and (c) 60%.

mass fraction of TiO ₂ /%	Atomic percentage/%						Ti/Ba
	C	S	Ti	O	Ba	Sum	
20	18.21	11.01	7.07	53.32	10.39	100.00	0.68
40	15.00	8.59	10.63	56.96	8.82	100.00	1.21
60	16.64	6.36	13.99	56.77	6.25	100.00	2.24

Table 2. Atomic percentage of the samples according to XPS analysis.

Samples	TiO ₂ mass ratio (%)	Colour coordinates			ΔE
		L*	a*	b*	
Barite	0	93.44	2.28	3.35	—
Rutile TiO ₂	100	97.04	−0.44	0.51	—
Barite-TiO ₂	20	95.34	0.30	1.05	1.93
Barite-TiO ₂	40	96.16	0.47	0.98	1.35
Barite-TiO ₂	60	97.34	0.13	0.66	0.66

Table 3. Colourimetric coordinates (L*, a*, and b*) and total colour difference (ΔE) between the TiO₂-coated barite composite pigments and rutile TiO₂.

which was used to compare the colour of two samples, ranges from 0.66 to 1.93. The ΔE value decreased as the TiO₂ mass ratio increased. These results indicate that the TiO₂-coated barite composite pigments display a similar visual colour to rutile TiO₂ because of the coating of TiO₂ particles on the barite particle surface.

The UV-vis absorption spectra of TiO₂-coated barite composite pigment (TiO₂ mass ratio was 60%), barite and TiO₂ were obtained and compared (See Fig. 4). There was less light absorbed by barite between 300 and 400 nm, whereas TiO₂ absorbed light of wavelengths below 400 nm. The TiO₂-coated barite composite pigments exhibited light absorption in a wavelength range from 200 to 400 nm. These pigments also show high light absorption at wavelengths of 300–400 nm, in complete contrast to barite but similar to TiO₂. The results indicate that the TiO₂-coated barite composite pigment has equivalent UV absorption and anti-UV properties, confirming that the barite is coated by TiO₂ particles with similar optical properties to TiO₂.

Compatibility with an organic matrix. To investigate the compatibility of the TiO₂-coated barite composite particles with an organic matrix, a dispersion experiment was performed. In this experiment, 1 g of composite particles was dispersed in 100 mL of kerosene to prepare a suspension, which was stirred for 30 min at a speed of 800 rpm. After stirring, a small amount of the suspension was taken to prepare samples. Images of the composite pigments in the kerosene medium are shown as Fig. 5. There are two types of particles in this experiment: the TiO₂-coated barite composite particles in Fig. 5(a), which were prepared by the mechanochemical method^{21,22} and the particles in Fig. 5(b), which were prepared by the hydrophobic aggregation method.

Clearly, the particle clusters in Fig. 5(a) are significantly larger than those in Fig. 5(b). In the kerosene medium, the TiO₂-coated barite composite particles prepared by the mechanochemical method agglomerate to form big aggregate particles with a size of 20–50 μm, which reflects their poor compatibility with the organic matrix. However, the particles observed in Fig. 5(b) possess a smaller particle size and exhibit good dispersion, indicating that the TiO₂-coated barite composite particles with a hydrophobic surface have good compatibility with the organic matrix.

Bonding properties of barite and TiO₂ particles. *Effect of barite and TiO₂ particles' surface hydrophobicity.* To investigate the effect of surface hydrophobicity and the carbon chain of the modifier on TiO₂ and barite particles and to further elucidate the bonding mechanism, TiO₂-coated barite composite pigments (the TiO₂ mass

Figure 4. UV-vis absorption spectra of (a) barite, (b) the TiO₂-coated barite composite pigments, and (c) rutile TiO₂.

Figure 5. Images of TiO₂-coated barite composite particles dispersed in a kerosene medium. The TiO₂-coated barite composite particles were prepared by (a) the mechanochemical method and (b) the hydrophobic aggregation method.

Samples	Mass ratio of TiO ₂ (R ₀)/%	Oil absorption/(g/100 g)	Hiding power/(g/m ²)	Relative hiding Power (R)/%	ΔR (R-R ₀)/%
1	60	11.40	16.61	66.04	6.04
2	60	11.20	15.37	71.37	11.37
3	60	12.56	14.82	74.02	14.02
4	60	14.48	12.08	90.81	30.81

Table 4. Pigment properties of the rutile TiO₂-coated barite composite particles. Sample 1 Barite + TiO₂, Sample 2 Modified barite + TiO₂, Sample 3 Barite + Modified TiO₂, and Sample 4 Modified barite + Modified TiO₂.

ratio was 60%) were prepared under the following conditions: The barite raw material had a contact angle of 22.5°, the modified barite material had a contact angle of 128.5°, the TiO₂ raw material had a contact angle of 33.2°, and the modified TiO₂ had a contact angle of 114.2°. The preparation details of the four samples are described in experiment section, Table 4 shows the pigment properties.

Among the four samples, Sample 4 exhibited the best pigment properties with a hiding power and a relative hiding power (R) of 12.08 g/m² and 90.81%, respectively. By contrast, the other three samples exhibited poor hiding properties with ΔR values ranging only from 6.04 to 14.04%, this result indicates the poor compositing of these samples. Based on these findings, it can be concluded that the composite performs effectively only when both the barite and TiO₂ surfaces exhibit hydrophobicity. Because the hydrophobicity of TiO₂ and barite particles

Figure 6. SEM images of (a) Sample 1, (b) Sample 2, (c) Sample 3 and (d) Sample 4.

Figure 7. Composite model of barite and TiO_2 particles with different surface hydrophobicities.

is obtained via modification with sodium stearate, the organic carbon chains of the modifier on the particle surface play an important part in the composite process. These observations demonstrate the hydrophobic interaction of barite and TiO_2 particles.

Figure 6 shows SEM images of the four samples. The clear view of the exposed surface of barite in Samples 1, 2, and 3 indicate that the barite particles in these samples have not been well coated by the TiO_2 particles. By contrast, the barite- TiO_2 composite particles in Sample 4 show an excellent coating morphology, where the barite particles are thoroughly coated by the TiO_2 particles. Figure 7 shows the composite model. The microstructure of the composite particles in the four samples can be used to explain the results in Table 4.

Figure 8. SEM images of barite-TiO₂ composite particles after sonication: (a) 100 W, 10 min; (b) 400 W, 10 min; and (c) 800 W, 10 min.

Figure 9. XRD patterns of (a) TiO₂, (b) barite and (c) the TiO₂-coated barite composite pigments.

Bonding strength analysis of barite and TiO₂ particles. The bonding strength between barite and TiO₂ particles is undoubtedly another key factor influencing the composite pigment properties. To evaluate the bonding strength between the barite and TiO₂ particles, an experiment based on the ultrasonic treatment of the TiO₂-coated barite composite pigments was carried out. First, the as-prepared TiO₂-coated barite composite pigments were mixed with ethanol-water (the mass ratio of ethanol to water was 1:4) to prepare a suspension, and then the suspension was ultrasonicated for 10 min at different powers with an ultrasonic oscillator. Finally, the samples were obtained after drying. Figure 8 shows the SEM images of the samples.

The barite particles were still coated by TiO₂ particles after the TiO₂-coated barite composite pigments were ultrasonicated at powers of 100 and 400 W. When the power increased to 800 W, only a small amount of the TiO₂ particles were removed from the barite particle surface. These results indicate that the bonding between barite and TiO₂ particles is strong enough, as the energy of ultrasonic vibration is substantially stronger than the Van der Waals forces of barite-TiO₂ particles²¹. This phenomenon can account for the similarity in pigment properties between the composite pigment and TiO₂. The aforementioned results also indicate that the bonding between TiO₂ and barite in the TiO₂-coated barite composite pigments is chemical or another physical combination with relatively large bonding energy.

XRD analysis. The XRD patterns of TiO₂, barite and TiO₂-coated barite composite pigments (see Fig. 9) show that the raw materials used in this study comprise pure barite (JCPDS 24–1035) and rutile crystal phase (JCPDS 21–1276). Only the diffraction peaks of barite and rutile appear at Fig. 9c, indicating that there is no new phase produced in the process of preparing the composite particles. Meanwhile, the barite and TiO₂ raw materials remain firmly in their complete crystal phases. Therefore, it can be inferred that the barite and TiO₂ particles form a mixed phase rather than undergoing a chemical reaction during the preparation process.

XPS analysis. The XPS analysis was carried out to prove the presence of TiO₂ particles in the TiO₂-coated barite composite pigment (the TiO₂ mass ratio is 60%), and also to elucidate the bonding mechanism. Figure 10 shows the wide-scan XPS spectra of the modified barite, modified rutile TiO₂, and TiO₂-coated composite pigments.

Figure 10. XPS spectra of (a) modified barite, (b) modified TiO_2 , and (c) the TiO_2 -coated barite composite pigments.

Figure 11. XPS narrow-scan spectra of (a) Ba 3d, (b) S 2p, and (c) Ti 2p.

The spectrum of the modified barite contains Ba 3d, S 2p and O 1s peaks, whereas the spectrum of modified TiO_2 shows Ti 2p and O 1s peaks, consistent with the composition of the raw materials. In contrast to the modified barite, the spectrum of the TiO_2 -coated barite composite pigment contains the Ti 2p peaks, suggesting that the barite surface was indeed coated with rutile TiO_2 .

Figure 11 shows the narrow-scan spectra of Ba 3d, S 2p, and Ti 2p in the modified barite, rutile TiO_2 and composite particles. In Fig. 11(a), the Ba 3d peaks appear at 780.40 eV and 780.75 eV, with the two peaks nearly overlapping. This finding indicates that the chemical state of barite was not changed during the compositing. The S 2p peaks in Fig. 11(b) appear at 169.10 eV and 168.95 eV and are assigned to SO_4^{2-} . This result indicates that SO_4^{2-} is not involved in any chemical reaction²⁹. Meanwhile, the peaks observed at 458.55 and 458.40 eV in the XPS spectrum of Ti 2p (see Fig. 11(c)) represent the $\text{Ti } 2p_{3/2}$ species of Ti^{4+} in TiO_2 ^{30,31}, confirming that the chemical state of TiO_2 was not changed. The abovementioned results show that no chemical reaction occurred between the barite and TiO_2 particles.

Figure 12. IR spectra of (a) sodium stearate, (b) the modified TiO₂, (c) the modified barite and (d) the TiO₂-coated barite composite pigments.

IR analysis. FTIR was used to illustrate the characteristic groups of sodium stearate, the modified rutile TiO₂, the modified barite, and the TiO₂-coated barite composite pigment (TiO₂ mass ratio is 60%). The results of FTIR analysis are shown in Fig. 12. In Fig. 12(a), the absorption peaks induced by the stretching vibrations of C-H bonds in the -CH₃ and -CH₂- groups appear at 2,917 and 2,850 cm⁻¹. Figure 12(b) displays peaks located at below 1,000 cm⁻¹, which are induced by the stretching vibrations of Ti-O-Ti bonds. These peaks are a characteristic rutile band^{32,33}. The absorption peak of hydroxyl groups (O-H) appears at 3,420 cm⁻¹ because of the intense hydration of unsaturated Ti⁴⁺. The absorption bands appearing at 2,917 and 2,849 cm⁻¹ are induced by the vibrations of C-H bonds³⁴. The aforementioned findings are attributed to the adsorption of the sodium stearate group (C₁₅H₃₅COOH or C₁₅H₃₅COO⁻) on the surface of the TiO₂ particles. Because of the existence of the O-H groups in TiO₂, it can be inferred that sodium stearate was adsorbed on the TiO₂ particle surface via its reaction with O-H. In Fig. 12(c), the absorption peaks of -CH₃ and -CH₂- at 2,917 and 2,850 cm⁻¹ are present, indicating that the modifier was adsorbed on the surface of the barite particles. In addition, the absorption peaks appearing in the range from 900 to 1,200 cm⁻¹ are typical SO₄²⁻ bands^{35,36} and the absorption bands of a terminal hydroxyl group (O-H) at 3,420 cm⁻¹ are induced by the hydration of SO₄²⁻^{37,38}. Based on the aforementioned results, sodium stearate was adsorbed on the surface of barite through an adsorption mechanism similar to that of TiO₂.

In Fig. 12(d), the characteristic adsorption bands of TiO₂ appear, and there are no new absorption peaks. This observation indicates that the TiO₂ coated the surface of the barite without chemical bonding. Meanwhile, the absorption bands of -CH₃ and -CH₂- also appear with a higher intensity; thus, the composite of TiO₂ and barite particles is induced by the hydrophobic interaction between the organic carbon chains on their surfaces. Since the interaction can induce the strong intertwining of the extended organic carbon chains on the surface of the particles, the particles are combined firmly with a binding energy that is much stronger than the Van der Waals force²⁴.

Composite mechanism and model. Figure 13 shows the composite model of the TiO₂-coated barite composite pigment. Based on the aforementioned research and analysis, the composite mechanism of the TiO₂-coated barite composite pigment prepared by hydrophobic aggregation can be described as follows:

First, as Fig. 13(a) and (b) show, the sodium stearate used as a modifier is adsorbed on the barite and TiO₂ particle surfaces via the reaction between C₁₅H₃₅COOH and the -OH groups on the surfaces of the TiO₂ and barite particles. The surfaces of the barite and TiO₂ particles are then covered by the organic groups of the modifier, and the hydrophobic groups are directed outward, thus increasing the hydrophobicity of particles. Second, the modified TiO₂ and barite are mixed and stirred in water, and the energy produced by stirring promotes the collision of the particles. Therefore, the distance between particles is reduced to such a range that the carbon chains adsorbed on the surfaces of particles are in contact. Then, the composite of barite and TiO₂ particles is formed by the interaction of the organic carbon chains (See Fig. 13(c)). Finally, the TiO₂-coated barite composite pigments with good pigment properties and hydrophobicity are prepared.

Several reasons may account for the good pigment properties and hydrophobicity of the TiO₂-coated barite composite pigments. Because of the TiO₂ coating on the surface of barite, the hydration hydroxyl groups on the surface of barite are covered. Meanwhile, the amount of -CH₃ and -CH₂- groups increase with the incorporation of the organic carbon chains on the surface of the composite particles.

Conclusions

Based on the surface hydrophobicity of barite and rutile TiO₂ particles induced by organic surface modification, rutile TiO₂-coated barite composite pigments with similar pigment properties to those of rutile TiO₂ were prepared by heterogeneous particle hydrophobic aggregation in a water medium. When the mass ratio of TiO₂ was 60%, the hiding power of the composite pigment was 12.08 g/m², which was equivalent to 90.81% of that of pure

Figure 13. Modification mechanism model of (a) rutile TiO₂, (b) barite and (c) composite model of the rutile TiO₂ and barite particles.

rutile TiO₂ pigment. Additionally, the TiO₂-coated barite composite pigment exhibited a strong surface hydrophobicity and similar optical properties to those of rutile TiO₂.

The TiO₂-coated barite composite pigment was characterized as TiO₂ particles uniformly and compactly coated on the barite particles surfaces. Notably, the coating structure could be formed only when both the surfaces of barite and TiO₂ particles had strong hydrophobicity. The barite and TiO₂ particles were combined by the association of the organic carbon chains on their surfaces without chemical reaction.

According to the reaction and bonding characteristics, we established the modification and composite model of the TiO₂-coated barite composite pigments prepared by the hydrophobic aggregation method.

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Author Contributions

Sijia Sun and Hao Ding wrote the main manuscript text, and Hong Zhou prepared Figures 1 and 10. All authors reviewed the manuscript.

Additional Information

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