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Research Article

Preparation and Characterization of Barite/TiO_2 Composite Particles

Hong Zhou, Mengmeng Wang, Hao Ding, and Gaoxiang Du

School of Materials Science and Engineering, China University of Geosciences, Beijing 100083, China

Correspondence should be addressed to Hao Ding; dinghao@cugb.edu.cn

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To make full use of barite mineral and obtain a kind of composite particles material which has the property of both barite and TiO_2, the composite particles material with TiO_2 coated on the surface of barite particle was prepared by the method of $TiOSO_4$ solution chemical hydrolysis and precipitation to form hydrolysis composite, removing the impurities of hydrolysis composite, drying, and calcination in this study. The results were evaluated by the covering power of composites. Composite structure and properties were characterized by means of XRD, SEM, FTIR, and XPS. The results showed that the surface of barite had been coated with rutile TiO_2 uniformly and compactly and the hiding power value and oil absorption value of the composite powder were 18.50 g/m^2 and 15.5 g/100 g, respectively, which had similar pigment performances to TiO_2. The results also showed that it was mainly the strong chemical bond between barite and TiO_2 that combined them firmly in barite/TiO_2 composite particle (B/TCP).

1. Introduction

The resource consumption, environmental pollution, cost ascension, and strong demand problems brought about during the production and application of TiO_2 limit its development seriously. To alleviate these problems and reduce the actual dosage of titanium dioxide, preparing white mineral/TiO_2 composite particle materials with similar pigment properties to TiO_2 caused a widespread concern. Many studies show that mineral surface-coated TiO_2 composite particles can be prepared by adding white mineral, such as kaolinite [1–4], wollastonite [5, 6], montmorillonite [7], sericite [8–10], tourmaline [11], and talc [12, 13] to the titanium salt solution [14]. To make titanium salt solution hydrolyzate (hydrated titanium dioxide, $TiO_2{\cdot}H_2O$) crystallize, the production needs to be calcined at about 600°C to 900°C. The studies above mainly researched the photocatalytic properties, pigment performance, and UV shielding performance of nanotitanium dioxide. As a result of the selected minerals which were more different from titanium dioxide in density, the prepared composites were easy to layer when mixed with other components and could not be used effectively.

Barite with the main component of $BaSO_4$ and similar density to titanium dioxide is a significant white nonmetallic mineral. Its high reservation, chemical stability, and low cost in China make it extensively applied in chemical raw materials, drilling mud raw materials, glass raw material, chemical fillers, and so on [15]. This is barite as mineral-TiO_2 composite particles substrate provides the basis. The density of barite was close to TiO_2, and both were 4.3 and 4.4 g/cm^3, and the oil absorption is low; therefore, preparing barite/TiO_2 composite powder paint is expected to obtain good effect.

There have been studies in preparing functional composite particles by coating metal oxide on surface of barite particles. Yang et al. [16] prepared Sb–SnO_2/$BaSO_4$ conductive powder by chemical precipitation method. Zhou [17] prepared barite loaded with nano-TiO_2 composites using $TiOSO_4$ and $TiCl_4$ as titanium source in process of methyl orange degradation. Wang et al. [18] prepared barite/TiO_2 composite particles by coating anatase TiO_2 on the surfaces of barite particles through mechanochemical method. These results showed that the prepared composite powders had certain kind of pigment performance and it was mainly the strong electrostatic attraction between barite and TiO_2 that combined them firmly and then formed B/TCP. Therefore,

the composites' pigment performance and the combination extent between barite and TiO_2 need to be improved.

To prepare barite coated with TiO_2 composite particles and combine them firmly, chemical precipitation method was used and the technology was studied in this paper. The preparation process conditions, pigment properties of composites, the structure of B/TCP, and the interaction mechanism between TiO_2 and barite particles were also investigated in this paper.

2. Experimental

2.1. Raw Materials and Reagents. The barite (particle size of less than 10 μm) used was provided by Antai Minerals Co., Ltd, Hebei Province, China. $TiOSO_4$ solution (concentration of 152 g/1000 mL) was produced by Jiaozuo Chemical Plant, Henan Province, China. Concentrated sulfuric acid and sodium hydroxide (analytical grade) were both purchased from Jingwen Huabo Commerce Center, Beijing, China.

2.2. Chemical Precipitation Coating Process. The process of preparing B/TCP by chemical precipitation method could be expressed as follows:

$$\text{Barite} \xrightarrow[\text{Preparation of core material}]{\text{Ultra-fine grinding}} \text{Fine barite powder} \xrightarrow[\text{Preparation of shell material}]{\text{Hydrolysis precipitation of titanyl sulfate}} \text{Barite/Titanium dioxide hydrate} \xrightarrow{\text{Calcined of hydrolyzate}} \text{B/TCP.} \quad (1)$$

Firstly, a certain amount of barite, grinding media, and distilled water were put into a stirred mill (Type GSDM-003, 3L, Beijing Gosdel Powder & Technology Co., Ltd.) and stirred at a speed of 1000 r·min^{-1}. The ratio of the grinding media to powder fed and the concentration of barite slurry were 4 : 1 and 45%, respectively. The particle size under different grinding time was measured by BT-1500 type centrifugal sedimentation particle size analyzer. Then the effects of grinding time on performance of B/TCP were studied.

Secondly, the barite powders after grinding for a certain time and distilled water were put into 800 mL of flask and stirred at a certain temperature. Then $TiOSO_4$ solution was added in five times. The pH value of the reaction solution was adjusted to 2.5 by adding H_2SO_4 and NaOH aqueous solution. When the reaction time was reached, the stir was stopped. The precipitate was washed with 70°C distilled water until it was neutral. After that the washed precipitate was filtrated and then dried.

Finally, the dried samples were calcined in muffle furnace at 800°C for 1 h. The as-prepared B/TCP samples were kept in a desiccator for characterization.

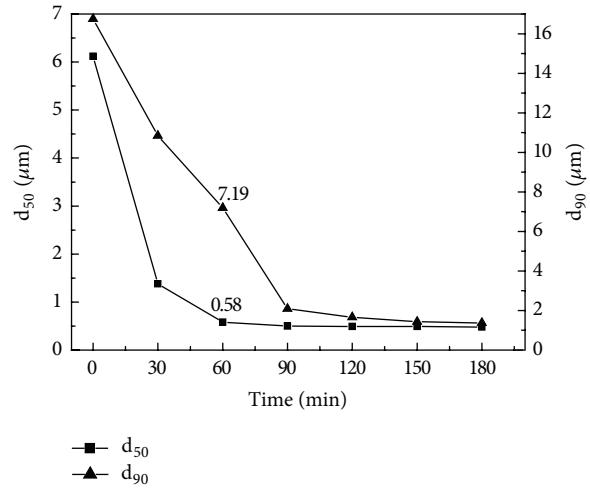

FIGURE 1: Effect of grinding time on granularity about d_{50} and d_{90} of barite.

2.3. Performance and Structure Research Means. The pigment properties of B/TCP were evaluated and the preparation conditions were optimized by measuring hiding power and oil absorption comprehensively. The hiding power (the minimum mass of pigment used to cover evenly a unit area of background surface when just hiding up its color, g·m^{-2}) and oil absorption value were measured according to the National Standards GB1709-79 and GB1712-79, respectively.

D/MAX 2000 X-ray powder diffractometer (XRD), made in Rigaku Company, was used to analyze the crystalline phase of B/TCP, and field emission scanning electron microscope, model JSM-7001F, made in Japanese Electronics Company, was used to observe the morphology of raw materials and composite particles. The infrared spectra of powder and the combined form between barite and titanium dioxide were measured by NICOLET 750 type infrared spectroscopy and ESCALAB 250 Xi type X-ray photoelectron spectroscopy spectrometer (XPS), respectively.

3. Results and Discussion

3.1. The Pigment Properties and Structure of B/TCP. The appropriate proportion between barite and TiO_2 was the premise of coating TiO_2 on barite effectively. Hydrolysis complex with barite under different grinding time was prepared. The preparation conditions were as follows: titanyl sulfate solution dosage : TiO_2 (included in $TiOSO_4$ solution) : barite = 1 : 1 (by mass), hydrolysis temperature 90°C, hydrolysis time 90 min, matrix slurry concentration of barite 1.0%, and the pH value about 2.5. Then B/TCP was prepared after hydrolysis complex was calcined at 800°C for 1 h. The effects of grinding time and granularity of barite on pigment properties of B/TCP were evaluated by hiding power value and oil absorption value comprehensively. The effects of grinding time on granularity of barite and pigment properties of B/TCP were shown in Figures 1 and 2, respectively.

Figure 1 showed that the granularity about d_{50} and d_{90} of barite decreased gradually with grinding time increasing,

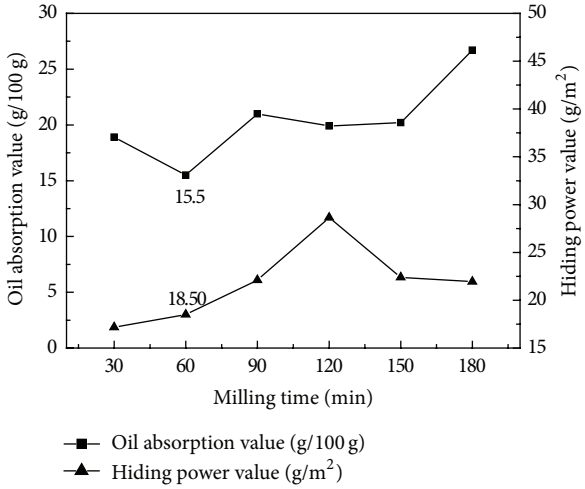

Figure 2: Effect of grinding time of barite on pigment properties of B/TCP.

indicating that the particle size was gradually refining. The granularity stabilized to a fixed value 90 min later, indicating that it might turn into a stable state. As shown in Figure 2, the hiding power value of B/TCP prepared first gradually increased and then declined, while the oil absorption value showed an upward trend. When the grinding time of barite reached 60 min, both of the hiding power value and oil absorption value of B/TCP prepared stabilized to a low value, showing that the pigment property was optimal. The granularity about d_{50} and d_{90} of barite prepared was 0.58 μm and 7.19 μm, respectively. The hiding power and oil absorption value of B/TCP prepared under optimal conditions were 18.50 g/m^2 and 15.5 g/100 g, respectively. The pigment property of B/TCP prepared was better than the results of B/TCP prepared through mechanochemical method by Wang et al. [18].

Figure 3 showed the SEM images of naked barite and B/TCP prepared with barite under different times.

3.2. Grinding Time. It was shown that the naked barite particle had regular square state and smooth surface without tiny covering, while the composite particle with regular state was covered with tiny covering in different degree. It could be deduced that composite particle was composed of barite particle as matrix and the tiny covering was TiO_2. Compared with the samples, it could be found that, after barite grinding for 30 min, 60 min, and 90 min, the composite particle had more TiO_2 which was uniformly and compactly covering its surface, in which after 60 min of grinding and TiO_2 coating, the composite particles had best covering effect. The result here corresponded to that of Figure 2, which also showed the relevance between structure and properties of B/TCP.

When barite grinding time continued to 120 min and 150 min, there was much area with barite naked on the surface of B/TCP, so TiO_2 covering degree was lower with worse covering effect. Apparently, the barite grinding time should not be too long during the preparation of B/TCP.

Table 1: EDS energy spectrum of naked barite and B/TCP.

Element	Weight percent	Atom percent
O	26.40	63.19
Mg	2.84	4.47
S	12.26	14.65
Ca	2.03	1.94
Ba	56.47	15.75
Total quality	**100.00**	
C	4.68	12.84
O	28.67	59.03
S	7.32	7.52
Ti	14.23	9.79
Ba	45.10	10.82
Total quality	**100.00**	

3.3. X-Ray Diffraction Analysis. The XRD patterns of naked barite, rutile and anatase TiO_2, and B/TCP prepared from barite-$TiOSO_4$ hydrolysis complex after calcination at different temperature were shown in Figure 4. It showed that the XRD peaks appearing at 2θ = 25.8, 26.8, 28.8, 31.5, and 43.0 were ascribed to that of barite; the XRD peaks appearing at 2θ = 27.4, 36.8, 42.6, 54.3, and 56.6° were ascribed to that of rutile TiO_2; the XRD peaks appearing at 2θ = 25.3, 37.8, 48.1, and 55.1° were ascribed to that of anatase TiO_2. Otherwise, little anatase TiO_2 diffraction peaks were generated when hydrolysis complex was calcined at less than 700°C, without rutile TiO_2 characteristic peak. It could be deduced that there was little $TiOSO_4$ hydrolysate on the surface of barite transformed into anatase crystalline phase. Almost all of TiO_2 on the surface of composite changed into rutile TiO_2 when calcined temperature increased to 750°C and 800°C and the diffraction peaks were strong. Meanwhile, the reflections of barite substrate decreased greatly, indicating that composite particle surface had mainly consisted of rutile TiO_2 and the barite surface was basically covered with TiO_2.

3.4. Scanning Electron Microscope and EDS Energy Spectrum Analysis. The SEM images of naked barite and B/TCP were shown in Figure 5, and the corresponding EDS spectrum analysis results were shown in Table 1.

Figure 5 showed that barite raw material was composed of regular square particles with smooth surface. It corresponded to the characteristic of orthogonal (oblique) crystal which existed in the form of thick plate-like, columnar, or granular aggregate. While B/TCP was composed of small TiO_2 particles uniformly and densely, it could be deduced that B/TCP was composed of TiO_2 coated with barite and TiO_2 was not aggregate. Obviously, barite was like a crystal core for the generated $TiO_2 \cdot H_2O$ growing and attached uniformly. And then the Barite-$TiO_2 \cdot H_2O$ composite particles were washed, stirred, filtered, and calcined at high temperature many times during the preparing process. But most of TiO_2 coating on the surface of barite did not drop off and had regular shape, compact arrangement, and fixed crystal type, indicating that TiO_2 and barite particle were combined firmly, which corresponded to XRD results.

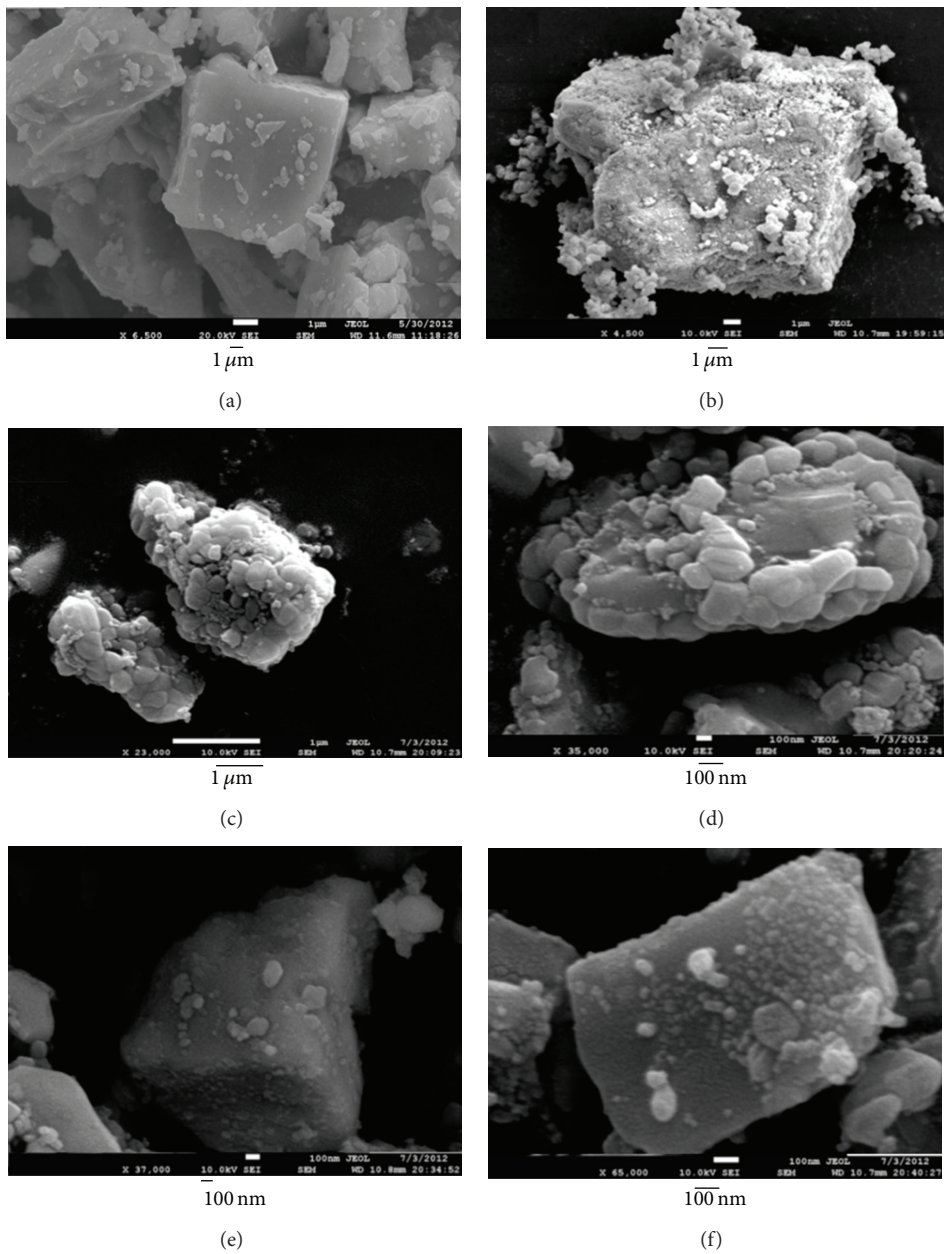

Figure 3: SEM images of naked barite (a), 30 min of grinding (b), 60 min of grinding (c), 90 min of grinding (d), 120 min of grinding (e), and 150 min of grinding (f).

As shown in Table 1, the EDS date of barite raw material was consistent with its elements, just a little Ca and Mg, indicating that it was pure. By comparing the EDS spectrum analysis of B/TCP and barite raw material, it could be found that the weight percent of S and Ba significantly decreased, while Ti increased obviously (the weight percent of 14.23%). It was deduced that quantity of TiO_2 was generated on surface of composites, which corresponded to XRD and the SEM results.

3.5. IR Spectrum Analysis. IR spectrograms of rutile TiO_2, B/TCP (prepared by calcining at 800°C for 1 h), and barite were shown in Figure 6. In the spectrogram of rutile TiO_2, the IR absorption bands at 674 cm^{-1} and 473 cm^{-1} corresponded to vibration of Ti–O. In the spectrogram of barite, the bands at 1177 cm^{-1}, 1115 cm^{-1}, and 1076 cm^{-1} were assigned to the asymmetric stretching vibration of S–O, resulting from threefold degeneracy of S–O. 983 cm^{-1} band was assigned to the symmetric stretching vibration of S–O, while bands at 635 cm^{-1} and 612 cm^{-1} corresponded to the bending vibration of S–O, which was also from the threefold degeneracy [19]. Therefore, it could be inferred that the IR spectrogram of this section mainly showed the inner vibration mode of SO_4 group. By comparing Figure 6 (a, b, and c) curve, it

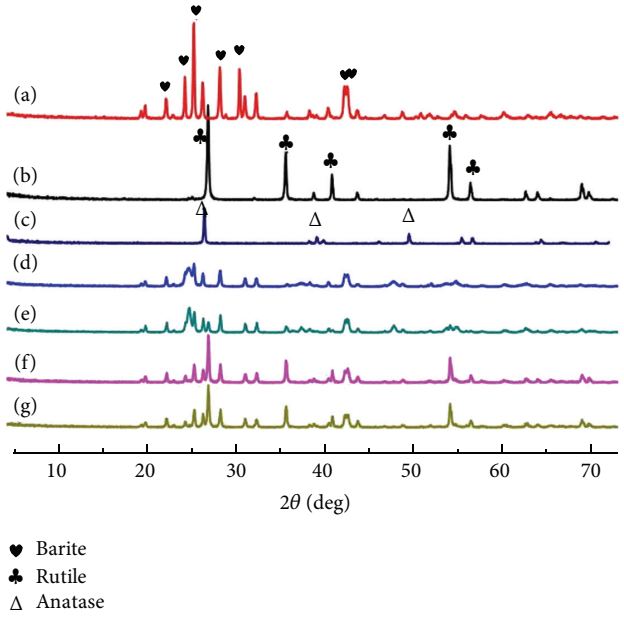

FIGURE 4: XRD patterns of the naked barite (a), rutile TiO_2 (b), anatase TiO_2 (c), and barite coated with TiO_2 powders ((d), (e), (f), and (g)) calcined at 600, 700, 750, and 800°C for 1 h.

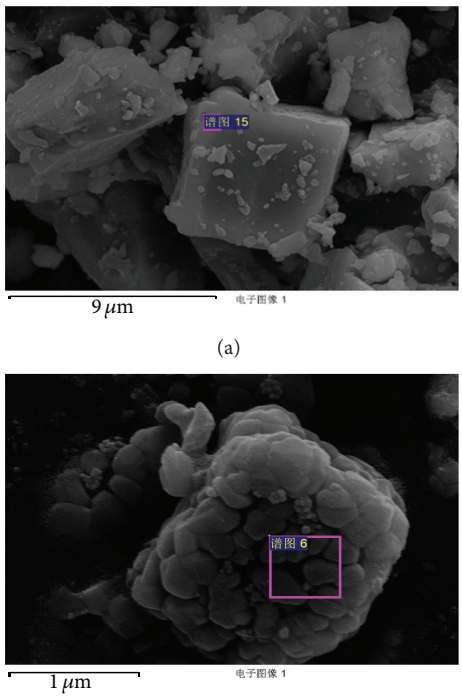

FIGURE 5: SEM images of naked barite (a) and B/TCP (b).

was shown that the bands of B/TCP at 883 cm^{-1}, 728 cm^{-1}, and 1440 cm^{-1} disappeared. Deducing from the above phenomenon, there were some free hydroxyls on the surface of B/TCP before being calcined and then they dropped off after being calcined. It could also be found that the peak at 612 cm^{-1} in Figure 6(b) turned wider than that in Figure 6(c), deducing that the banding form of Ba^{2+} and hydroxyl on the surface of B/TCP might have changed and a new chemical bond Ti–O–Ba was formed.

3.6. XPS Analysis. As Figures 7, 8, and 9 show, to prove the binding energy of each main characteristic element before and after B/TCP being formed and deduce Ti–O–Ba chemical bond formed, the naked barite, rutile TiO_2, and B/TCP were characterized with XPS under a CuKα-radiation, a power of 150 W, and a background pressure of 6.5×10^{-10} mbar including all elements spectrum diagram and Ba, S, and Ti elements spectrum diagram. The binding energy of Ba_{3d} in naked barite was 779.61 eV, while it changed into 780.74 eV in TiO_2-coated barite powders. Therefore, the binding energy of Ba_{3d} shifted to a higher value about 1.13 eV, indicating that the chemical environment around Ba atom changed. Moreover, the binding energy of S_{2p} in raw barite and Ti_{2p} in rutile TiO_2 was 169.00 eV and 458.44 eV, respectively. However, the value changed into 170.02 eV and 458.46 eV, respectively, in B/TCP. Comparing with the binding energy in barite and rutile TiO_2, the binding energy of S_{2p} and Ti_{2p} shifted to a higher value about 1.02 eV and 0.02 eV. From the change above, it could be indicated that the chemical environment around S atom in barite changed apparently after barite covering with TiO_2. The binding energy shift of Ti_{2p} was lower, deducing that it still combined with O firmly in the form of Ti–O bond.

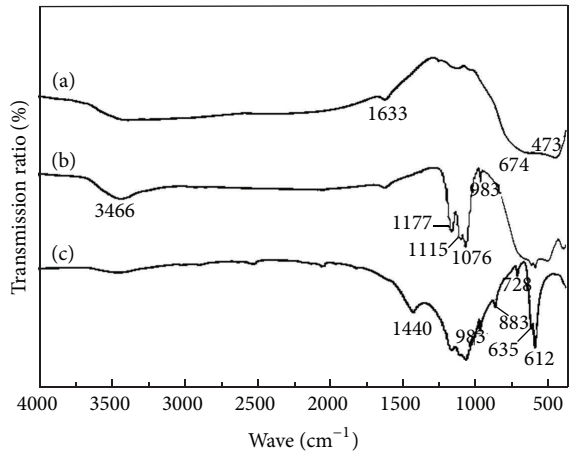

FIGURE 6: IR spectrum of samples: (a) the IR spectrogram of TiO_2; (b) the IR spectrogram of B/TCP; and (c) the IR spectrogram of barite.

As a result of some free hydroxyl groups around Ba atom and Ti atom which exist in barite-$TiO_2 \cdot H_2O$, Ba atom and Ti atom were combined by dropping off hydrogen and hydroxyl, forming Ti–O–Ba bond. The chemical shift is generated due to the environmental changes of atoms, which is mainly from the potential energy changes caused by valence electron transfer. Valence electron transfer is closely related to the electronegativity of corresponding element [20]. The inner electrons of the atoms are mainly attracted through Coulomb force by nucleus, which makes the electron have a certain binding energy. Meanwhile, the inner electron is

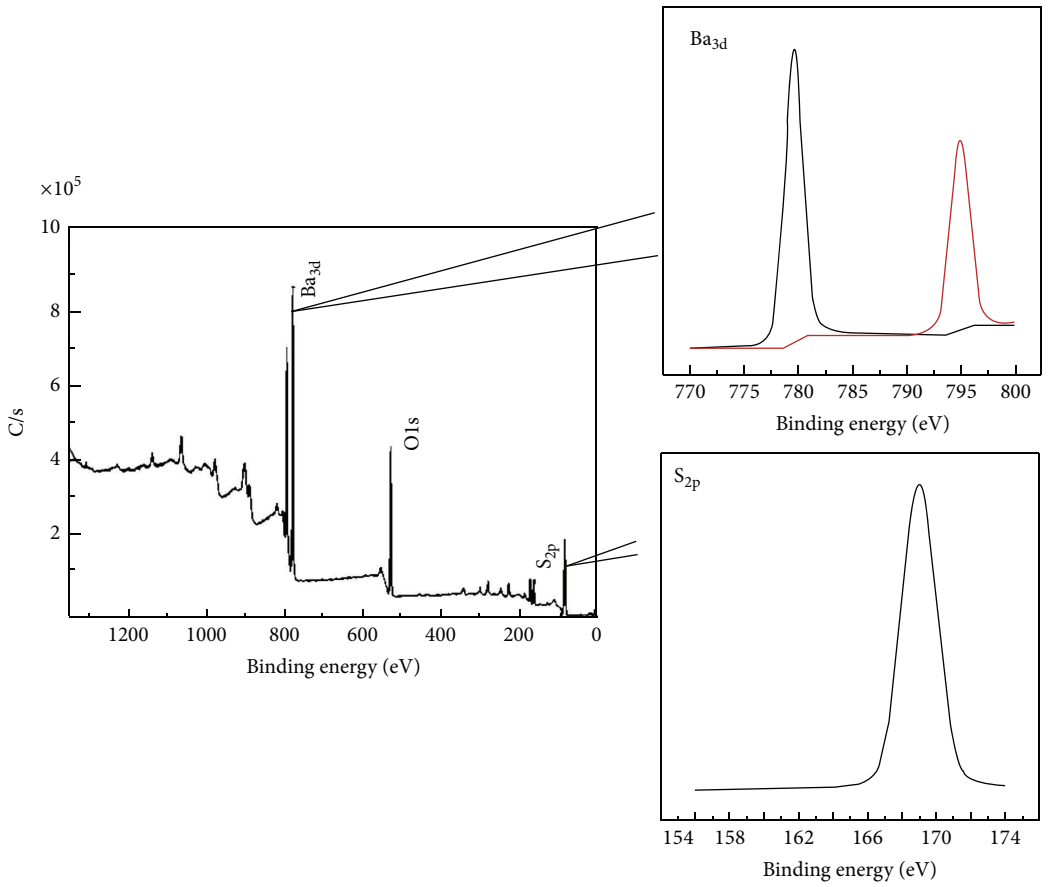

Figure 7: XPS spectrum of all elements of barite and XPS spectrum of Ba and S.

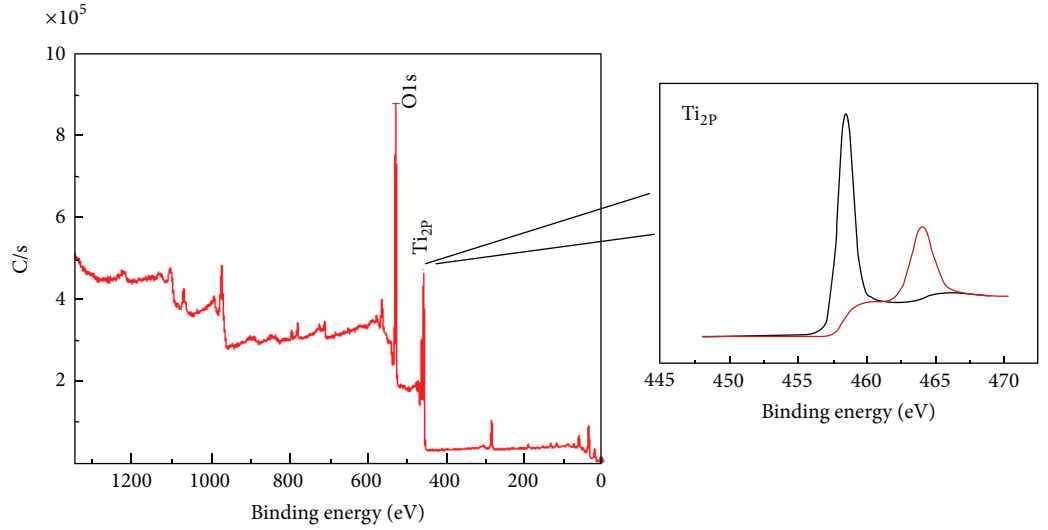

Figure 8: XPS spectrum of all elements of rutile TiO_2 and XPS spectrum of Ti.

shielded by the outer electron. Therefore, when the valence electrons shift to the large electronegativity atom, whose electron concentration is increased, the shielding effect is enhanced and the binding energy is decreased. On the contrary, the binding capacity will increase. Due to the larger electronegativity of Ti than that of Ba, the electron around Ba transfers to O–Ti, and then the electron concentration around Ti is increased, the shielding effect is enhanced, and the binding energy is decreased, while the binding energy of Ba is increased.

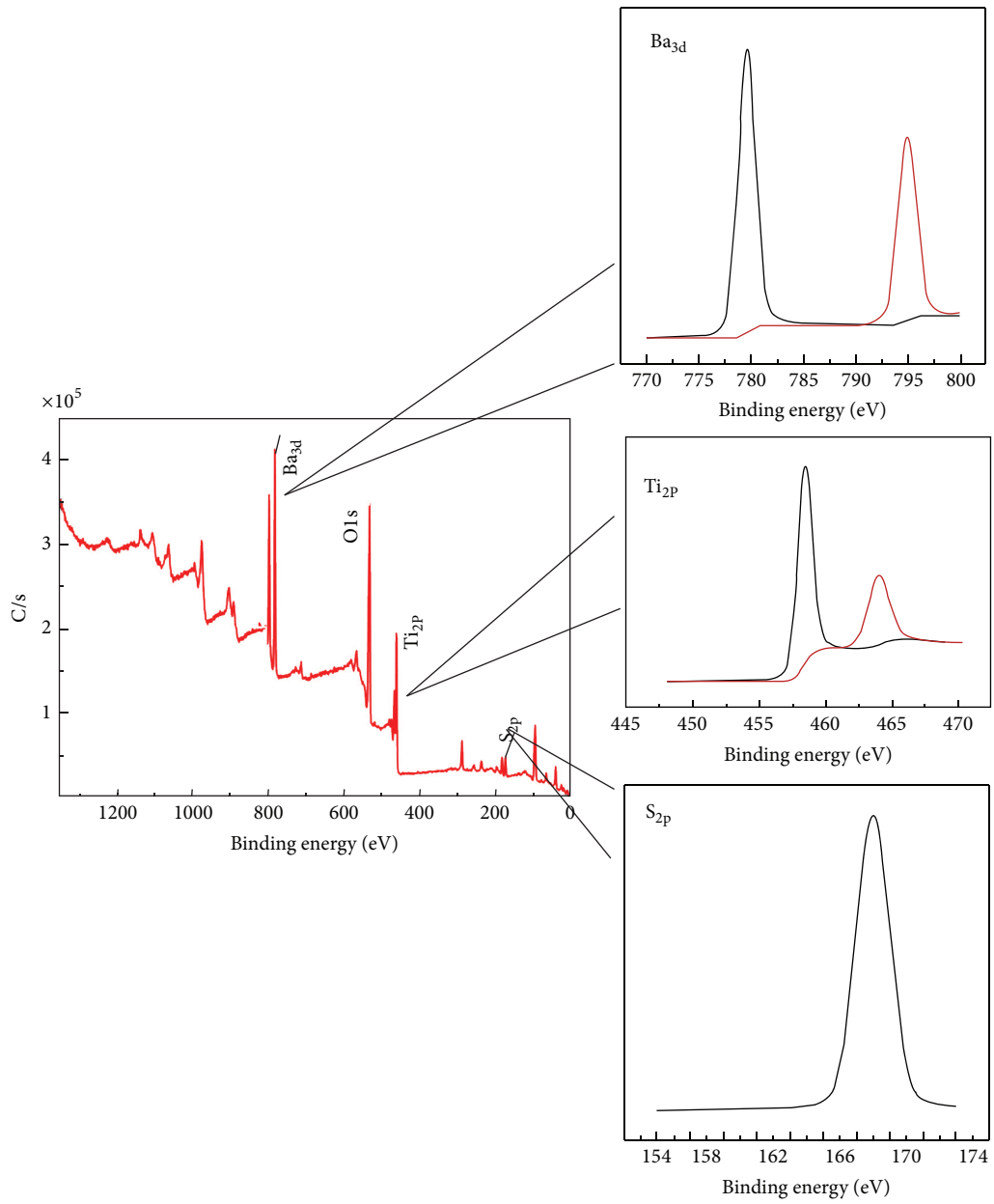

Figure 9: XPS spectrum of all elements of B/TCP and XPS spectrum of Ba, S, and Ti.

4. Conclusion

(1) B/TCP was prepared through $TiOSO_4$ hydrolysis, $TiO_2{\cdot}H_2O$ depositing and coating on the surfaces of barite, and composite particles calcined method in $TiOSO_4$ hydrolysis system including barite. The results showed that the composite powder had similar pigment performances with titanium dioxide and the oil absorption value and hiding power value were 15.5 g/100 g and 18.50 g/m^2, respectively.

(2) The structure and properties of B/TCP were influenced greatly by the granularity of barite and the calcined temperature of hydrolysis complex. The composite particles with TiO_2 coating on the surface of barite uniformly and compactly were prepared when the granularity about d_{50} and d_{90} of barite was 0.58 μm and 7.19 μm, respectively. When the calcined temperature of hydrolysis complex was over 700°C, the TiO_2 on the surface of composite particle was rutile crystalline.

(3) By analyzing the results of IR and XPS, we deduce that barite and TiO_2 were combined with Ti–O–Ba chemical bond in B/TCP, which made TiO_2 coat on the surface of barite uniform, compact, and firm.

(4) In the process of preparation of B/TCP, the pigment performance of B/TCP would be more better, when TiO_2 coated on the surface of barite the more uniformly and compactly, and they combined the more firmly. Therefore, the results show that this study is very useful to improve the pigment performance of B/TCP.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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