Effects of Structural Factors of Hydrated TiO\textsubscript{2} on Rutile TiO\textsubscript{2} Pigment Preparation via Short Sulfate Process

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The structural factors such as crystal structure, particle size distribution and impurity content of hydrated TiO\textsubscript{2} had great effects on the structures and pigment properties of the rutile TiO\textsubscript{2}. The rutile TiO\textsubscript{2} white pigment was prepared via the Short Sulfate Process from low concentration industrial TiOSO\textsubscript{4} solution. In order to produce rutile TiO\textsubscript{2} pigment with good structures and excellent pigment properties, the crystal size of the hydrated TiO\textsubscript{2} should be controlled less than 8.9 nm and as close as possible to 7.9 nm, which could effectively promote the phase transformation and crystal growth of the rutile TiO\textsubscript{2}. The appropriate particle size distribution of hydrated TiO\textsubscript{2} had obvious effects on obtaining rutile TiO\textsubscript{2} with narrower particle size distribution and near 0.20 \( \mu \text{m} \). It was best to adjust the hydrolysis conditions to reduce the specific surface area of the hydrated TiO\textsubscript{2} so as to reduce the iron ion impurity adsorption.

In the material science, the material’s properties are determined by their structural factors, such as the crystal structure, phase composition, chemical composition, and so on, its essence is the reflection of material structure theory. And the structural factors would be determined by the preparation process and controlling conditions, which would ultimately determine the properties and applications of the materials. Titanium dioxide (TiO\textsubscript{2}) is the third largest commercial inorganic chemicals, either in anatase or rutile polymorphs, and due to its excellent properties such as higher refractive index, smaller crystal size, better optical properties and chemical inertness, it has become the most widely used white pigments, used in many fields such as coatings, paints, paper, fibers, cosmetics, sunscreen products, chemical catalysis, electronic materials and so forth\textsuperscript{1–3}. Titanium dioxide white pigment is commercially prepared by either chloride process or sulfate process. In recent year, the market demand of titanium dioxide increases by about 3% every year. In 2019, the global titanium dioxide production capacity was 8,685,000 tons, the production capacity was of 3,845,000 tons and the output was of 3,137,200 tons in China in 2019, and the output of the sulfate process accounting for 93.6% in China. The core step for titanium dioxide production via the sulfate process is the hydrolysis of the titanyl sulfate solution. The hydrolysis process would undergo a series of complex physical and chemical reactions, and the hydrolysis parameters and conditions would have great effects on the structure of the hydrolysis products (hydrated TiO\textsubscript{2}, also named metatitanic acid), and the structure and quality of hydrated TiO\textsubscript{2} would ultimately determine the structure and properties of the titanium dioxide pigment. And the thermal hydrolysis reactions of industrial TiOSO\textsubscript{4} solution include nucleation, crystal growing, polymerization, agglomeration, aggregation and precipitation, accompanied by hydrolysis precipitation of crystalline TiO\textsubscript{2} ions via olation and oxolation reaction\textsuperscript{4}. Researches show that the hydrated TiO\textsubscript{2} is colloidal particles, formed by nuclei growing and aggregating, and eventually forming the secondary aggregated particles with the particle size of 10–200 \( \mu \text{m} \). Many researchers have widely investigated the hydrolysis process and conditions, effects of the additives and hydrolysis parameters on the products, as well as properties and applications of titanium dioxide\textsuperscript{5–16}. Urakaev \textit{et al}. investigated the homogeneous nucleation and growth of monodispersed spherials of sulphur and hydrated titanium dioxide of anatase modification by a new coherent optical method for measurement of the relative scattering coefficient based on alternative use of laser radiation of various wavelengths\textsuperscript{17}. Ultrasonic technology was used to pretreat hydrated TiO\textsubscript{2} slurry before washing, which showed that the removal effect of iron impurities in hydrated TiO\textsubscript{2} was better and the effect of washing water...

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The specific surface area of hydrated TiO₂ was measured on the surface and pore size distribution
of hydrated TiO₂. The as-prepared hydrated TiO₂ was washed with water, bleached and filtered, then whipped to
solution with a deionized water uniformly. The slurry was doped with the rutile calcining seed (5%, as to TiO₂, wt
%), zinc salt (ZnO of 0.26%), potassium salt (K₂O of 0.50%) and phosphate salt (P₂O₅ of 0.11%), then calcined in a
muffle furnace in the air atmosphere. The calcining conditions was as the following: firstly from room
temperature raising to 420 °C in 60 min and holding for 30 min at 420 °C, secondly from 420 °C to 780 °C in 60 min and
holding for 60 min at 780 °C, and lastly from 780 °C to 870 °C in 120 min and holding for 40 min. Then the rutile
TiO₂ pigment powder was obtained after cooling and grinding by the three head grinder. The different concentra-
tion of industrial TiOSO₄ solution was conducted at 155 g/L, 161 g/L, 167 g/L, 173 g/L, 180 g/L, and the obtained
hydrated TiO₂ samples were marked as A, B, C, D, E, the rutile TiO₂ samples after salt treatment and calcination
were denoted as A1, B1, C1, D1, E1, respectively.

The crystal structures of hydrated titanium dioxide and rutile TiO₂ were determined by the XRD analysis (X'
Pert³ Powder, PANalytical), and the crystal size \( L(101) \) for the anatase crystal plane (101) of hydrated TiO₂ and
\( L(110) \) for rutile TiO₂; crystal plane (110) was calculated according to Scherrer equation (Eq. A), where \( K \) was the
constant (0.98906), \( \lambda \) was the wavelength of Cu Kα, (0.15418 nm), \( \beta \) was the full width at half maximum intensity
(FWHM) of crystal plane for XRD peak in radians, and \( \theta \) was the Bragg's diffraction angle, respectively. The rutile
content \( X_R \) was calculated according to Eq. B, where \( I_α \) and \( I_R \) represented the integrated intensity of the anatase
(101) main peak and the rutile (110) main peak, respectively.

\[
\text{Crystal size: } L = \frac{K\lambda}{\beta \cdot \cos \theta} \quad (A)
\]

\[
\text{Rutile phase content: } X_R = \frac{I_R}{0.8841I_α + I_R} \quad (B)
\]

Particle size distribution (PSD) test was carried out on a Malvern particle size analyzer (Malvern Zetasizer Nano
ZS90). The specific surface area of hydrated TiO₂ was measured on the surface and pore size distribution
instrument (3H-2000PS1, Beishide, China). The \( S_{BET} \) of the hydrated TiO₂ samples were calculated by the BET
multi-point method according to the \( N_2 \) adsorption–desorption curves. The UV–vis diffuse reflection spectra
were obtained on a ultraviolet visible spectrophotometer with integral ball accessories (U-4100, Hitachi). The
crystal structure of the obtained hydrated TiO₂ had great impacts on the XRD patterns of hydrated TiO₂.

Results and Discussions

Crystal structure. The crystal structure of the obtained hydrated TiO₂ had great impacts on the crystal
structure of titanium dioxide pigment, and would ultimately affect the pigment properties of titanium dioxide. The
XRD patterns of the as-prepared hydrated TiO₂ series were showed in Fig. 1, and the XRD patterns for rutile TiO₂
in Fig. 2. The crystal size for anatase \( L_{(101)} \) of hydrated TiO₂, and the crystal size for rutile \( L_{(110)} \), the rutile content
\( X_R \) and pigment properties for rutile TiO₂ white pigment were listed in Table 1.

In the hydrolysis system to produce titanium dioxide pigment, the hydrolysis intermediates (also named
hydrated TiO₂, or metatitanic acid) would absorb a large amount of water and sulfate anion to form the crystalline
structure with anatase phase, due to the presence of a large number of sulfate anion in the hydrolysis system, with
the molecular structure as $\text{H}_2\text{TiO}_3\cdot\text{H}_2\text{O}$. In Fig. 1, all the XRD patterns of the hydrated TiO$_2$ samples were clearly consistent with the standard anatase TiO$_2$ phase (JCPDS 21–1272), without any other crystal phase diffraction peaks, showing with only the anatase phase. The hydrated TiO$_2$ was anatase phase with low crystallinity due to their wide flat diffraction peaks and low diffraction intensity. The crystal size $L_{(101)}$ for hydrated titanium dioxide ranged from 8.42 nm to 7.10 nm. Hydrated titanium dioxide was transformed into rutile TiO$_2$ structure after salt treatment and calcinations, and the rutile crystal phase structure was consistent with the standard rutile TiO$_2$ (JCPDS 21–1276). Due to the difference of crystal size, particle size distribution and impurity content for metatitanic acid, there was a small deviation in the rutile crystallization process during the calcination process, resulting in a small deviation in the XRD pattern. The rutile content ($X_R$) increased gradually with the decreasing of the crystal size $L_{(101)}$ of hydrated titanium dioxide (as listed in Table 1). The negative linear correlation between $X_R$ and $L_{(101)}$ were shown in Eq. (1). In the equation, $R$ represented as the correlation coefficient and $SD$ represented as the standard deviation.

![Figure 1. XRD patterns for the hydrated TiO$_2$.](image1)

![Figure 2. XRD patterns for the rutile TiO$_2$ pigments.](image2)

| Hydrated TiO$_2$ | $L_{(101)}$(nm) | Rutile TiO$_2$ | $X_R$ (%) | $L_{(110)}$(nm) | TCS | SCX | Jasn |
|------------------|----------------|--------------|-----------|----------------|-----|-----|------|
| A                | 8.42           | A1           | 98.5      | 124.2          | 1780| 2.25| 94.54|
| B                | 8.14           | B1           | 98.8      | 134.1          | 1820| 2.56| 94.86|
| C                | 7.83           | C1           | 99.1      | 142.4          | 1840| 3.18| 95.17|
| D                | 7.57           | D1           | 99.4      | 147.6          | 1810| 2.64| 94.93|
| E                | 7.10           | E1           | 99.9      | 158.3          | 1700| 2.19| 94.68|
| R930             | /              | /            | /         | /              | 1910| 3.12| 94.52|

Table 1. Crystal size, rutile content and pigment properties for hydrated TiO$_2$ and rutile TiO$_2$ pigment.
When the crystal size of hydrated TiO$_2$ was small, it was easier to transform into rutile TiO$_2$ crystalline by surface atom diffusion during calcination process due to its higher crystal surface energy. In the calcination process, the phase transformation from anatase to rutile was mainly through the surface atomic diffusion, in order to use the atomic reconstruction to reduce the energy of the crystal and form a stable rutile structure. When rutile crystal nucleus was formed, the TiO$_2$ crystal ions continuously aggregated and grew on the newly formed rutile crystal nucleus through surface atom diffusion, which would make the rutile titanium dioxide crystal growing. And at the same conditions, the smaller crystal size of hydrated TiO$_2$ needed the lower calcination conditions and strength for crystal phase transformation from anatase to rutile. In order to meet the requirement of rutile content for rutile TiO$_2$ production ($X_R > = 98\%$), the anatase crystal size of the hydrolyzed hydrated TiO$_2$ should be controlled below 8.89 nm. However, when the crystal size of hydrated TiO$_2$ was too small and with obvious colloidal properties, the calcined particles would be easily sintering to form larger rutile titanium dioxide particles, resulting in deteriorating the rutile TiO$_2$ pigments properties.

The negative linear mathematical relationship of crystal size between $L_{(110)}$ for the rutile TiO$_2$ and $L_{(101)}$ for the hydrated TiO$_2$ was as the following, Eq. (2).

$$L_{(110)} = 338.79 - 25.28 \times L_{(101)}, \quad R = 0.9943, \quad SD = 1.595$$

(2)

From Eq. (2), as crystal size decreasing of hydrated TiO$_2$, it would be easy to transform hydrated TiO$_2$ to rutile structure and promote the atomic diffusion in the calcination process based on the high surface energy of hydrated TiO$_2$, which would make the phase transformation and crystal growth of rutile TiO$_2$ easier and obtain the larger rutile crystals. On the other hand, it would be easier to cause the sample sintering and agglomerate to form larger crystals, which would be beneficial for the crystal size of hydrated TiO$_2$ being too small.

The pigment properties of rutile TiO$_2$ pigments (also named initial product) were mainly determined by its crystal structure, particle size and its distribution. The chromatic power $(TCS)$ of the calcined rutile TiO$_2$ products ranged from 1700 to 1840. Without coating post-treatment, the $TCS$ values for the rutile samples were lower than the reference sample R930 which was with coating post-treatment. The $TCS$ of the samples increased firstly and then decreased as the crystal size of hydrated TiO$_2$ decreasing gradually. The mathematical relationship between $TCS$ and $L_{(101)}$ was as the following equation, Eq. (3).

$$TCS = -11415.26 + 3354.25 \times L_{(101)} - 212.26 \times L_{(101)}^2, \quad R^2 = 0.9959, \quad SD = 4.983$$

(3)

Equation (3) showed quadratic linear relationship with high fitting degree. After taking the derivation, it showed that the maximum value of $TCS$ was of 1836.2 (about 1840) when the crystal size of hydrated TiO$_2$ was of 7.90 nm, indicating that the pigment properties of rutile TiO$_2$ were partly determined by the structure of hydrated TiO$_2$. And the crystal size of hydrated TiO$_2$ could be controlled in an appropriate range by adjusting the hydrolysis conditions such as the number and quality of the hydrolysis seeds, concentration of TiOSO$_4$ solution and hydrolysis time, which could effectively improve the product pigment properties. It could also approximately predict the pigment properties according to crystal size of hydrated TiO$_2$ under certain conditions.

The blue phase (SCX) of the rutile pigment showed a similar changing trend as that of $TCS$, which was gradually increasing from 2.25 to 3.18, and then decreasing to 2.19. It was harmful for phase transformation from anatase to rutile and rutile crystal growth during calcination process when the crystal size of hydrated TiO$_2$ was too large or too small. Because of the inconsistent phase transformation and growth of rutile crystal, it was easier to cause uneven growth of rutile TiO$_2$ crystalline grain, ultimately reducing its sintering resistance and the SCX value. The brightness index $(Jasn)$ of the calcined products was better and higher than that of the reference sample R930 (94.52). The $Jasn$ also showed the same changing trend as that of $TCS$, increasing gradually to 95.17 at first and then decreasing to 94.68.

Appropriate crystal structure and suitable crystal size of hydrated TiO$_2$ were helpful to promote the phase transformation from anatase to rutile and the rutile crystal growth during the calcination process to obtain good rutile TiO$_2$ crystalline structure, resulting in proper crystal size of the rutile titanium dioxide. The integrity of rutile crystal structure ensured its high refractive index and scarcely any sintering particles, which could improve the calcination process and obtain rutile TiO$_2$ with suitable particle size distribution and better crystal structure. All these influencing factors were helpful to improve the rutile pigment properties.

### Particle size distribution and impurity iron content

The particle size distribution (PSD) of the rutile titanium dioxide also had important influences on the pigment properties. Because the $TCS$ of the rutile TiO$_2$ was related to the light scattering coefficient ($S$) and the light absorption coefficient ($K$), the larger of $S$ value and the smaller of $K$ value, the larger of $TCS$, and the better of the covering power and whiteness of the titanium dioxide pigment. Generally, in order to improve the $S$ value, the particle size of the pigment should be controlled in the range of 0.15–0.35 $\mu$m in the visible light range, and the amount and content of titanium dioxide particles should be maintained as higher as possible in the range about 0.2 $\mu$m. The average particle size ($D_{av}$), particle polydispersity ($Pdi$), relative scattering force ($R_S$) and impurities content of the calcined rutile TiO$_2$ pigments were showed in Table 2.

The $D_{av}$ of hydrated TiO$_2$ ranged from 0.782 $\mu$m to 1.130 $\mu$m. The polydispersity ($Pdi$) was used to characterize the particle size distribution of the mono-dispersity particles, and the smaller the value was, the more concentrated particle size distribution was. The $Pdi$ value was the index indicating the wide and narrow of particle size distribution, the smaller the $Pdi$ value was, the narrower the $PSD$ was. The $Pdi$ of hydrated TiO$_2$ ranged from 0.132 to 0.475, and sample C was the smallest with the narrowest $PSD$. The $D_{av}$ of the calcined rutile TiO$_2$ ranged from...
0.238 µm to 0.372 µm, with the Pdi value ranging from 0.107 to 0.387, of which sample C1 had the narrowest PSD with Pdi of 0.107. It showed that the Pdi value of titanium dioxide prepared by hydrated TiO₂ with smaller Pdi value was also smaller than the others (Table 2), which indicated that narrower PSD of hydrated TiO₂ was beneficial to obtain TiO₂ powders with narrower PSD. The Pdi values for hydrated TiO₂ and rutile TiO₂ were met with the following mathematical relationships.

\[
P_{\text{di}} = -0.00554 + 0.82955 \times P_{\text{di,HA}} \quad R = 0.9975, \quad SD = 0.00893
\]

The relationships of Pdi showed positive linear correlation (Eq. (4)). Narrower PSD of hydrated TiO₂ was beneficial to control the crystal phase transformation and crystal growth of rutile TiO₂ in a suitable uniform range during the calcination process. When the PSD of hydrated TiO₂ was narrower, as the particle size was more uniform in the calcining process, and the properties and compositions of the active sites of anatase TiO₂ in the phase transformation and crystal growth were closer, by atomic diffusion and crystal growth on the particle's surface, the obtained calcined rutile particles were uniform. Ultimately, the obtained calcined rutile TiO₂ was with narrower Pdi values, as the particle size was more uniform in the calcining process, which ultimately deteriorated the pigment properties. When the PSD of hydrated TiO₂ was narrower, the PSD of the calcined rutile TiO₂ became wider due to the inconsistent diffusion process and crystal growth during the calcining process, which ultimately deteriorated the pigment properties.

| Hydrated TiO₂ | D<sub>AV</sub> (nm) | Pdi | S<sub>BET</sub> (m²/g) | Fe % | Rutile TiO₂ | D<sub>AV</sub> (nm) | Pdi | Wt, % (0.15–0.30 µm) | Fe % | ZnO % | K₂O + Na₂O % | P₂O₅ % | RS % |
|---------------|---------------------|-----|----------------------|------|-------------|---------------------|-----|-------------------|------|--------|-------------|---------|-----|
| A             | 1130                | 0.433 | 275                  | 0.0042 | A1          | 339                 | 0.362 | 66.8              | 0.0040 | 0.2295 | 0.1522      | 0.1025   | 97.8 |
| B             | 976                 | 0.341 | 256                  | 0.0022 | B1          | 307                 | 0.265 | 71.4              | 0.0021 | 0.2283 | 0.1519      | 0.1021   | 98.4 |
| C             | 782                 | 0.132 | 243                  | 0.0012 | C1          | 238                 | 0.107 | 78.2              | 0.0011 | 0.2272 | 0.1526      | 0.1018   | 99.2 |
| D             | 887                 | 0.369 | 267                  | 0.0034 | D1          | 321                 | 0.303 | 69.7              | 0.0033 | 0.2279 | 0.1531      | 0.1020   | 97.9 |
| E             | 1029                | 0.475 | 282                  | 0.0052 | E1          | 372                 | 0.387 | 64.1              | 0.0050 | 0.2284 | 0.1534      | 0.1022   | 97.1 |
| R930          | /                   | /    | /                    | /     | R930        | /                   | /    | /                 | /     | /       | /           | /       | 100  |

Table 2. Effect of particle size distribution and impurities content of hydrated TiO₂ on rutile TiO₂ pigment.

Figure 3. UV–vis diffuse reflection spectra for the rutile TiO₂ pigments.

The UV–vis spectra for the rutile TiO₂ pigments were showed in Fig. 3. The absorption spectra for all the samples were consistent, there was a strong absorption in the wavelength region less than 402.4 nm, and the difference of absorption intensity was not significant. This part of absorption corresponded to the intrinsic absorption of rutile titanium dioxide, which was the energy absorbed by the electron transition from the valence band of
titanium dioxide to the conduction band (the intrinsic forbidden band width, 3.08 eV). The fine fluctuation of the absorption spectra might be caused by different sizes of the rutile crystals.

The SEM photographs for the rutile samples were shown in Fig. 4. All the particles showed rutile TiO₂ morphologies with clearly crystal contour, and the high crystalline was consistent with the XRD analysis. The particle size ranges from 70 nm to 300 nm, and the main average particle size was of about 120 nm. During the calcination process, the smaller particles might congregate together to form a larger one due to re-crystallization because its higher surface energy and crystal growth drive, resulting in larger particle size and larger DₐV, as showing in Table 2. It could be seen that the larger and wider the particle size of hydrated TiO₂ was, the wider PSD of rutile TiO₂ products was, resulting in poor pigment properties, as listed in Tables 1 and 2. And sample C1 was with the narrowest PSD and the smallest Pdi, and it confirmed that the appropriate PSD for the hydrated TiO₂ would improve the crystal growth and PSD for rutile TiO₂. This also proved that appropriate particle size and narrow PSD of hydrated TiO₂ were conducive to obtaining narrower and uniform particle size distribution of rutile TiO₂, and reducing sintering phenomena for the particles, which would lead to improve the pigment properties. The regular crystallographic perfection, good and complete morphology, proper PSD for TiO₂ was all beneficial to improve pigment properties.

Figure 4. SEM photographs for rutile TiO₂ pigment.
The TEM photograph for sample C1 was showed in Fig. 5. The crystal profile of sample C1 was clear, and the particle uniformity was good. The average size was about 240 nm, which was consistent with the particle size test results. The size of particles was different, which might be related to the slow hydrolysis rate and uneven hydrolysis process of TiOSO₄ solution. Better particle morphology and particle size distribution would contribute to the improvement of the pigment performances.

Because the hydrolyzed hydrated TiO₂ was with small size of crystal and aggregates, large specific surface area and stronger colloidal properties, the impurities were easy to be adsorbed on and brought out by hydrated TiO₂. As the adsorbed amount of colored impurities was one of the key factors affecting the structure of titanium dioxide, it was of great importance to improve pigment properties by controlling the adsorbed impurities in an appropriate range. The iron impurity was the main colored impurity, and when the content exceeded the limited range (commonly less than 30 ppm for rutile TiO₂ and less than 90 ppm for anatase TiO₂), it would cause the rutile samples yellowing and sintering, which would seriously worsen the pigment performances. The main impurities content including Fe, ZnO, K₂O + Na₂O and P₂O₅ of the rutile TiO₂ pigments were listed in Table 2, and the content of these impurities was low, which had little effect on the properties of the rutile TiO₂ pigments. The specific surface area (SBET) was a key factor that affecting the adsorbed amount of impurities. The absorbed content of iron ions gradually increased with the increasing of the SBET for hydrated TiO₂ (as showed in Table 2). The relationship between the adsorption amount of impurity iron (% Fe) and the SBET of hydrated titanium dioxide was as the following equation.

\[
\% Fe = -0.02371 + 1.01839 \times 10^{-4} \times SBET, \quad R = 0.9948, \quad SD = 0.0001869
\]

The % Fe had positive linear correlation with the SBET of hydrated TiO₂. The SBET of the hydrated TiO₂ should be as small as possible in order to control the % Fe. The SBET of hydrated TiO₂ was connected with the hydrolysis conditions and operational parameters. When the hydrolysis conditions were well controlled, the hydrolysis reaction was conducted more uniform, the precipitated hydrated TiO₂ particles were more well-distributed and the formed aggregates were with narrower particle size distribution and relative smaller SBET. At the same time, the colloidal properties of hydrated TiO₂ would be weakened by increasing the hydrolysis temperature and prolonging the hydrolysis time, which could reduce the SBET and adsorption amount of impurity iron, resulting in better pigment properties. In addition, it was also great important that hydrated TiO₂ with narrower particle size distribution and smaller SBET, which could be conducive to reduce the subsequent washing water consumption, shorten the washing time and reduce the washing strength and cost.

Conclusions

The rutile TiO₂ pigments were prepared through thermal hydrolysis by authigenic seed method via Short Sulfate Process. The structural factors such as crystal structure, particle size distribution, impurity content of the iron ion and specific surface area of the hydrated titanium dioxide had great important impacts on the crystal structure, pigment properties and PSD of the rutile TiO₂, and there had also an internal influencing relationship among these factors, these factors influenced and determined each other. Suitable crystal size and crystal structure of the hydrolyzed hydrated TiO₂ were helpful to promote the phase transformation from anatase to rutile and crystal growth of rutile TiO₂, and it was also related to the rutile content, crystal size and pigment properties of rutile TiO₂, satisfying with mathematical regression correlation. It was advisable to control the crystal size of hydrated to be less than 8.9 nm and close to 7.9 nm, which could obtain rutile TiO₂ with good crystal structure which could reduce the sintering of the particles and enhance the pigment performances for rutile TiO₂ pigments. The appropriate particle size and particle size distribution of hydrated TiO₂ had obvious effects on the particle size distribution, polydispersity and relative scattering force of the rutile TiO₂ particles. The adsorption amount of
impurity iron ions was greatly affected by the S_{BET} of hydrated TiO_2, and there was a correlation relationship between them. Rutile titanium dioxide pigments with good structure, regular morphology and excellent pigment properties could be prepared by controlling the hydrolysis conditions to obtain hydrated TiO_2 with the particle size distribution as much narrower as possible, and lower impurity content of iron. Appropriate structural factors of hydrated TiO_2 were helpful to prepare titanium dioxide with excellent pigment properties.

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References
1. Buxbaum, G. & Pfaff, G. Industrial Inorganic Pigments, Third, Completely Revised Edition, Chapter 2.1 Titanium Dioxide, 51-81 (WILEY-CHY Verlag GmbH & Co. KGaA, Weinheim 2005).
2. Jalava, J. P. The use of an exact light-scattering theory for spheroidal TiO_2 pigment particles. Particle & Particle Systems Characterization 23, 159–164, https://doi.org/10.1002/ppsc.200601025 (2006).
3. Wang, Y., Li, J., Wang, L., Xue, T. & Qi, T. Preparation of rutile titanium dioxide white pigment via doping and calcination of metatitanic acid obtained by the NaOH molten salt method. Industrial & Engineering Chemistry Research 49, 7693–7696, https://doi.org/10.1021/ie070147 (2010).
4. Santacassia, E., Tonello, M., Storti, G., Pace, R. C. & Carra, S. Kinetics of titanium dioxide precipitation by thermal hydrolysis. Journal of Colloid and Interface Science 111, 44–53, https://doi.org/10.1016/0021-9797(86)90065-6 (1986).
5. Sathyamoorthy, S., Honsloeh, M. J. & Moggridge, G. D. Influence of stirrer speed on the precipitation of anatase particles from titanyl sulphate solution. Journal of Crystal Growth 223, 225–234, https://doi.org/10.1016/S0022-0248(01)00619-4 (2001).
6. Przepera, A., Jablonski, M. & Wisniewski, M. Study of kinetics of reaction of titanium raw-materials with sulfuric-acid. Journal of Thermal Analysis And Calorimetry 40, 1341–1345, https://doi.org/10.1007/BF02546898 (1993).
7. Tian, C. X. Internal influences of hydrolysis conditions on rutile TiO_2 pigment production via short sulfate process. Materials Research Bulletin 103, 83–88, https://doi.org/10.1016/j.materresbull.2018.03.025 (2018).
8. Garg, A. et al. Photocatalytic degradation of bisphenol-A using N, Co codoped TiO_2 catalyst under solar light. Scientific Reports 9, 765, https://doi.org/10.1038/s41598-019-43858-w (2019).
9. Kim, E. J. et al. Thorn-like TiO_2 nanorays with broad spectrum antimicrobial activity through physical puncture and photocatalytic action. Scientific Reports 9, 13697, https://doi.org/10.1038/s41598-019-40016-0 (2019).
10. Wang, J. Y., Liu, B. S. & Nakata, K. Effects of crystallinity, [001]/[101] ratio, and Au decoration on the photocatalytic activity of anatase TiO_2; crystals. Chinese Journal of Catalysis 40, 403–412, https://doi.org/10.1016/S1872-2067(18)31742-2 (2019).
11. Di, T. M., Zhang, J. F., Cheng, B., Yu, J. G. & Xu, J. Hierarchically nanostructured porous TiO_2 (B) with superior photocatalytic CO_2 reduction activity. Science China. Chemistry 61, 344–350, https://doi.org/10.1007/s11426-017-9174-9 (2018).
12. Szilagyi, I., Konigsberger, E. & May, P. M. Characterization of chemical speciation of titanyl sulfate solutions for production of titanium dioxide precipitates. Inorganic Chemistry 48, 2200–2204, https://doi.org/10.1021/acs.inorgchem.8b01722 (2009).
13. Grzmił, B., Grela, D. & Kic, R. Effects of processing parameters on hydrolysis of TiOSO_4, Polish Journal of Chemical Technology 11, 15–21, https://doi.org/10.2478/v10026-009-0030-1 (2009).
14. Grzmił, B., Grela, D. & Kic, R. Formtion of hydrated titanium dioxide from seeded titanyl sulphate solution. Chemical Papers 63, 217–225, https://doi.org/10.1007/s11696-009-0009-7 (2009).
15. Tian, M. et al. Mechanism of synthesis of anatase TiO_2 pigment from low concentration of titanyl sulfuric-chloric acid solution under hydrothermal hydrolysis. Journal of the Chinese Chemical Society 67, 277–287, https://doi.org/10.1007/s12220-019-00007 (2020).
16. Xin, W. H. et al. A facile preparation strategy for TiO_2 spheres by direct hydrolysis. ChemNanoMat 5, 1263–1266, https://doi.org/10.1002/cnma.201900567 (2019).
17. Urakaev, F. K. et al. Kinetics of homogeneous nucleation of monodisperse spherical sulfur and anatase particles in water-acid systems. Journal of Crystal Growth 205, 223–232, https://doi.org/10.1016/S0022-0248(99)00236-5 (1999).
18. Zhao, G. et al. Use of ultrasound in the washing process of titania pigment production: Water saving and process optimization. Chemical Engineering Communications 203, 1207–1215, https://doi.org/10.1080/0098645.2016.1160226 (2016).
19. Ohenoka, J., Iikikainen, M. & Ninnimaki, J. Effect of operational parameters and stress energies on the particle size distribution of TiO_2 pigment in stirred media milling. Powder Technology 234, 91–98, https://doi.org/10.1016/j.powtec.2012.09.038 (2013).
20. Baneshi, M., Genome, H., Komiyama, A. & Maruyama, S. The effect of particles size distribution on aesthetic and thermal performances of polydispersed TiO_2 pigmented coatings: Comparison between numerical and experimental results. Journal of Quantitative Spectroscopy & Radiative Transfer 113, 594–606, https://doi.org/10.1016/j.jqsrt.2012.02.006 (2012).
21. Zhang, W., Ou, C. R. & Yuan, Z. G. Precipitation and growth behaviour of metatitanic acid particles from titanium sulfate solution. Powder Technology 315, 31–36, https://doi.org/10.1016/j.powtec.2017.03.047 (2017).
22. Jalil, M. M., Davoudi, K., Sedigh, E. Z. & Farrokhpay, S. Surface treatment of TiO_2 nanoparticles to improve dispersion in non-polar solvents. Advanced Powder Technology 27, 2168–2174, https://doi.org/10.1016/j.apt.2016.07.030 (2016).
23. Tian, C. X., Huang, S. H. & Yang, Y. Anatase TiO_2 white pigment production from unenriched industrial titanyl sulfate solution via short sulfate process. Dyes and Pigments 96, 609–613, https://doi.org/10.1016/j.dyepig.2012.09.016 (2013).
24. Tian, C. X. Calcination intensity on rutile white pigment production via short sulfate process. Dyes and Pigments 133, 60–64, https://doi.org/10.1016/j.dyepig.2016.05.034 (2016).
25. Chen, H. L., Wang, Y. R. & Shi, J. Preparation of monodisperse superfine titanium dioxide particles and size control. Acta. Physico-Chimica Sinica 17, 713–717, https://doi.org/10.3866/PKU.WHXB20010809 (2001).

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Author contributions
Congxue Tian wrote the manual manuscript text and prepared all the figures and all the tables. And Congxue Tian reviewed the manuscript.

Competing interests
The author declares no competing interests.
Additional information

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