

Research Article

Surface Organic Modification of TiO_2 Powder and Relevant Characterization

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Surface organic modification was conducted to TiO_2 with modifiers to improve the dispersity and comparability of pigment TiO_2 in application system by adjusting particle surface characteristics. Then, modification effects were characterized according to the changes in wetting contact angle and activation index of TiO_2 before and after modification. Moreover, the modification mechanisms of sodium stearate and sodium oleate were studied by analyzing the characteristics of TiO_2 surface functional groups in modification system and effects of modifiers. The results showed that, after being wet-processed with sodium stearate and sodium oleate, TiO_2 could turn from surface hydrophilic to inductive hydrophobic with controllable degree. The wetting contact angle of modified TiO_2 increased from 7° to 125.6° and 121.3° , respectively. The dispersity of TiO_2 in organic medium was stronger than that in inorganic medium. The modifiers formed absorption with chemical property on TiO_2 particle surface, so the inductive hydrophobicity of surface was stable.

1. Introduction

Titanium dioxide (TiO_2) is metallic oxide with excellent physical and chemical properties. Its particle in submicron scale ($0.2\text{--}0.3\ \mu\text{m}$) is the component of the best white pigment; nanometer TiO_2 (less than $100\ \text{nm}$) is excellent photocatalytic material. Therefore, TiO_2 draws general attention. With properties of high refractive index, no toxicity, strong stability, high brightness, high covering power, and so forth, TiO_2 has been widely used in fields of coating, plastic, papermaking, printing ink, chemical fiber, and so forth [1–7]. As the photocatalyst, nanometer TiO_2 is applied in fields of water and air purification [8–11], breaking down procedures of organic pollutant degradation [12, 13], medical waste treatment [14, 15], and so forth. Actually, above properties and their roles are dependent on the control over the purity, crystal form, and size distribution of TiO_2 powder in synthesis and preparation. Moreover, the postprocessing is also important in optimizing the surface morphology and compatibility with application system. Therefore, the processing for TiO_2 powder is necessary when improving the application performance.

Micro-nano TiO_2 is poor in compatibility with high polymer material because of small grain size, high surface energy, and, especially, strong hydrophilia for surface hydroxylation. Actually, the bad dispersity and agglomeration of TiO_2 in organic system impede its pigment performance or photocatalytic performance. However, this problem can be solved by improving the dispersity of TiO_2 in application system. In the way of particle surface modification, the surface wettability can be adjusted and the morphology of surface functional groups be changed. Guosheng et al. conducted surface organic modification to nano- TiO_2 particle with silane coupling agent. The results show that TiO_2 turns from surface hydrophilic to surface hydrophobic [16]. In addition, TiO_2 particle was also modified with sodium stearate and polyethylene glycol, lauryl sodium sulfate and triethanolamine, and sodium hexametaphosphate by Gang et al. [17], Xihai et al. [18], Hui [19], Ding et al. [20–22], and Weng et al. [23], respectively. All of these studies show that the dispersity of TiO_2 improves in corresponding medium. This work also indicates that the application effects of modifiers with carboxylic in structure are more ideal among above modifiers [24–26]. Except for surface modifier, it is also

important to make preassessment for TiO_2 modification effects. At present, the surface modification of powder is mainly evaluated by measurement with contact angle [27, 28] and activation index [29]. However, the modification effects and stability of changed surface wettability cannot be evaluated. Moreover, the modification mechanism cannot be reflected with the interaction between modifier and TiO_2 particle. This work conducted surface modification to TiO_2 particle in micrometer scale by wet-modification with modifiers, sodium stearate, and sodium oleate. Suspension was prepared with TiO_2 powder and water in the weight ratio of 1:1 and heated to and fixed at 65°C . Then, appropriate dosage of modifier was added to adjust pH value of modifier equal to or smaller than 7. The modified suspension was obtained after 30 minutes of heat preservation and constant stirring. After drying and dispersing the modified suspension, modified TiO_2 powder can be obtained. Then, the modification effects of TiO_2 were characterized according to the changes of wetting contact angle and activation index in different liquid mediums before and after modification. Finally, the modification mechanisms of TiO_2 were studied by testing the infrared spectrums and analyzing the morphology of surface functional groups before and after modification with sodium stearate and sodium oleate.

2. Experiments

2.1. Raw Materials and Reagent. TiO_2 used in tests was anatase-type titanium oxide powder manufactured by Henan Billions Chemicals Co., Ltd. In sample test, the particle size was median diameter (d_{50}) of $0.37\ \mu\text{m}$; specific surface area was $6.125\ \text{m}^2/\text{g}^{-1}$; whiteness was 98.80%; covering power was $12.99\ \text{g}/\text{m}^2$; oil absorption was $24.40\ \text{g}/100\ \text{g}$; and water-wetting contact angle was 7° .

The organic modifiers in test, sodium stearate and sodium oleate, were all chemically pure reagents provided by Beijing JingweiHuabo Co., Ltd. The reagents should be disposed as 5% water solution by heating.

2.2. Process of TiO_2 Organic Modification. Surface modification for TiO_2 was conducted by water suspension wet surface modification. Suspension was prepared with TiO_2 powder and water in weight ratio of 1:1 (solid content 50%) and heated to constant temperature (65°C). Then, the modifier solution was added to TiO_2 water suspension by ratio to adjust the pH value equal to or less than 7. Modified suspension was obtained after thermal insulation and constant stirring for 30 minutes. TiO_2 powder can be obtained after drying and dispersing the modified suspension.

2.3. Performance and Structural Characterization

2.3.1. Wetting Contact Angle. Contact angle (θ) refers to the included angle between gas-liquid surface and solid-liquid surface (including liquid) in the junction of three phases, gas, liquid, and solid. As the physical quantity quantitatively reflecting the wetting degree on solid surface, contact angle can represent the change in surface characteristics of TiO_2 before and after modification. Therefore, contact angle can be

used to determine the modification effects. When measuring the angle, the sample to be tested should be pressed as the solid slice with smooth surface. Then, contact angle gauge (JC2000D, Shanghai powereach digital technology equipment Co. Ltd.) should be used to measure and take photo of wetting contact angle.

2.3.2. Activation Index. Activation index refers to the percentage of powder floating on the water-gas interface accounting for the total volume after mixing the modified powder in water. Particles with surface hydrophobicity may float on the interface in the comprehensive action of adhesive force, gravity, buoyancy, water pressure, and so forth in moist periphery of three phases. The stronger the surface hydrophobicity of particle is, the greater the adhesive force in moist periphery and the larger the floating trend will be. Therefore, the floating powder can intuitively reflect the surface modification effects.

2 g modified sample was correctly weighed and placed in pear-shaped funnel with 200 mL water. After oscillation and stewing, the sedimentation at bottom in hierarchy was introduced to beaker for drying and weighing. The activation index of sample H could be calculated by following formula:

$$H = \frac{\text{Sedimentation quantity in total quality}}{\text{Total quality}} \times 100\%. \quad (1)$$

2.3.3. Infrared Spectroscopy. Infrared spectroscopy analysis can be used to detect various keys in molecule, structure of functional group, and binding characteristics of different parts in composite materials. After compressing the sample to be tested and KBr, Spectrum 100 infrared spectrometric analyzer manufactured by Shanghai PerkinElmer Co., Ltd. was used for infrared spectrometry and analysis. The scanning scope of instrument was $4000\ \text{cm}^{-1}$ – $400\ \text{cm}^{-1}$, and the resolution ratio was $3\ \text{cm}^{-1}$.

3. Results and Discussion

3.1. Change of Modified TiO_2 Wetting Contact Angle with Modifiers and Dosage. Figure 1 shows the influences of modifier dosage on the contact angle of TiO_2 wetted by water after TiO_2 particles were modified with sodium stearate and sodium oleate. Figure 2 shows the microscopic image of wetting contact angle.

According to Figure 1, the contact angle continuously enlarged with the increase of modifier dosage after TiO_2 is modified with sodium stearate and sodium oleate. The angles are 125.6° (modified with sodium stearate) and 121.3° (modified with sodium oleate), larger than 90° , critical between hydrophile and hydrophobicity, when modifier dosage is 1.5%. The contact angle of TiO_2 is 7° before modification. Obviously, TiO_2 surface has turned from strong hydrophilia to hydrophobicity after modification. However, the wetting contact angle on TiO_2 surface decreases in small range when the dosage further increases. The results show that both modifiers can change the wettability of TiO_2 surface. Moreover, the hydrophobicity formed in modification can be controlled with modifier dosage. In other words, the wettability on

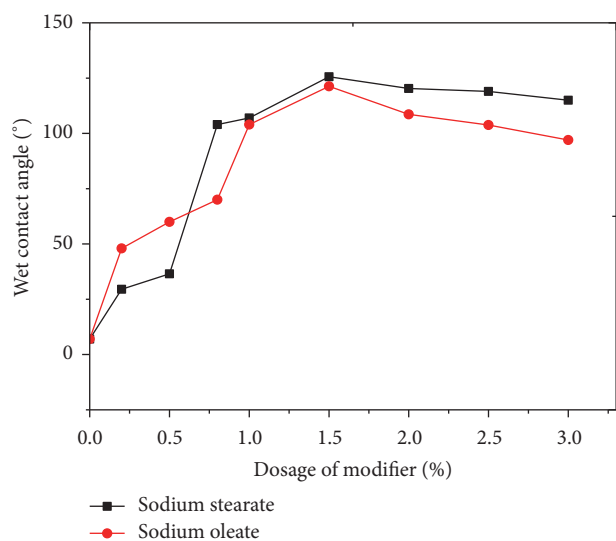


FIGURE 1: The wetting contact angle of modified TiO_2 in water.

TiO_2 particle surface and its degree are controllable. Figure 2 intuitively reflects the changes in Figure 1.

In this work, TiO_2 was modified with sodium stearate and sodium oleate (in dosage of 1.5%), respectively. Figure 3 shows the contact angles of modified product and unmodified TiO_2 wetted by water, absolute ethyl alcohol, and kerosene. It can be seen that the contact angle of modified TiO_2 wetted by absolute ethyl alcohol is about 21° , while the angle wetted by water is larger than 120° (see Figure 1). This means that the hydrophilia of TiO_2 with alcohol is stronger than that with water because alcohol has double characters of organics and water. Therefore, modified TiO_2 with surface strong hydrophobicity has stronger wetting action than water. The wetting contact angle of modified TiO_2 in kerosene (organic nonpolar solvent) is slightly smaller than that in ethyl alcohol (less than 20°). In other words, the hydrophilia of modified TiO_2 in kerosene is much stronger than that in alcohol. It means that the surface of modified TiO_2 particle has stronger organic nonpolarity. Moreover, the above results further specify that modifiers form the effective absorption on the surface of TiO_2 particle, so the particle turns from surface hydrophilia to hydrophobicity. Figure 3 also shows that the contact angle of unmodified TiO_2 wetted by alcohol and kerosene is about 20° larger than that wetted by water. In other words, the wetness degree of alcohol and kerosene is lower than water. This means that unmodified TiO_2 has strong surface hydrophilicity.

Before and after modification, wetting contact angle of TiO_2 particles changed in different mediums. This means that TiO_2 particle has extremely strong hydrophilia which may turn to strong hydrophobicity after organic modification. The wettability of modified TiO_2 particle in organic medium is stronger than that in inorganic medium, which is beneficial to the improvement of dispersity in organic medium.

3.2. Changes in Activation Index of Modified TiO_2 . Activation index is an important index evaluating modification. The

stronger the hydrophobicity TiO_2 particles are, the larger the activation index will be. Figure 4 shows the changes in activation index of TiO_2 powder modified by sodium stearate and sodium oleate. According to the figure, the activation index of modified TiO_2 greatly increases with the dosages of sodium stearate and sodium oleate increasing from 0% to 1.5% and from 0% to 1%, respectively. Moreover, the activation index reached the maximum, 98.6% and 89.7%, when the dosages of sodium stearate and sodium oleate were 1.5% and 1%, respectively. However, with the further increase of sodium stearate and sodium oleate, the activation index of TiO_2 may slightly decrease or keep stable. This is because the surface modification of TiO_2 is incomplete if the modifier dosage is little, so the activation index is small. With the increase of modifier dosage, however, the unimolecular coverage is realized with modifier on the surface of TiO_2 to make the modifier dosage saturated. At this time, the activation index is the maximum. If the modifier dosage further increases, multilayer coats will form on the surface of TiO_2 particles to make some types of group outward and reduce the hydrophobicity of TiO_2 . Therefore, the activation index will decrease. The change of activation index shows that after modifying the sodium stearate and sodium oleate of TiO_2 , the hydrophilia on surface will turn to strong hydrophobic effects. This is obviously the interaction between TiO_2 particle and modifier molecule, as well as the coating on the surface of TiO_2 [30, 31].

This means that TiO_2 surface turns from hydrophilia to strong hydrophobicity after being modified with sodium stearate and sodium oleate. This is obviously the result of TiO_2 particle and modifier molecule covering TiO_2 surface. Above results are consistent with the analysis on contact angle test.

3.3. Function Mechanism of Modifiers and TiO_2 Particle

3.3.1. IR Analysis on TiO_2 Modified with Sodium Stearate and Sodium Oleate. The mechanism of TiO_2 surface showing strong hydrophobicity can be further understood and hydrophobicity stability be determined by studying the properties of interaction between modifiers, sodium stearate and sodium oleate and TiO_2 surface. Therefore, the infrared spectroscopies were measured for sodium stearate and sodium oleate, as well as TiO_2 modified by these two modifiers. Figures 5 and 6 show the measurement results.

Figure 5 shows that there are symmetrical and dis-symmetrical characteristic absorption peaks of $-\text{CH}_2-$ at $2,917\text{ cm}^{-1}$ and $2,849\text{ cm}^{-1}$ in the infrared spectroscopy of sodium stearate (see Figure 5(a)). Moreover, there is characteristic absorption peak of $-\text{CH}_3$ at $2,956\text{ cm}^{-1}$ and stretching absorption peaks of carbonyl ($\text{C}=\text{O}$) and carboxyl ($\text{COO}-$) at $1,557\text{ cm}^{-1}$ and $1,470\text{ cm}^{-1}$. All of these reflect the structural characteristics of sodium stearate. Compared with raw material of sodium stearate and TiO_2 , there are absorption peaks at $2,996\text{ cm}^{-1}$ and $2,885\text{ cm}^{-1}$ in the infrared spectroscopy of modified TiO_2 . This is obviously the characteristics of $-\text{CH}_2-$ and $-\text{CH}_3$, showing that sodium stearate has attached to TiO_2 surface.

According to the comparison, the absorption peak of modified TiO_2 at $1,504\text{ cm}^{-1}$ resulted from the displacement

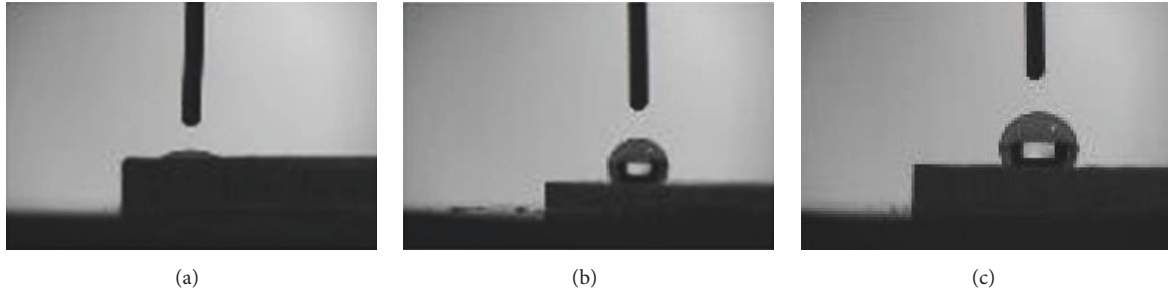


FIGURE 2: Microscopic image of wet contact angle of TiO_2 . (a) Wet contact angle of TiO_2 , (b) wet contact angle of modified TiO_2 with sodium stearate, and (c) wet contact angle of modified TiO_2 with sodium oleate.

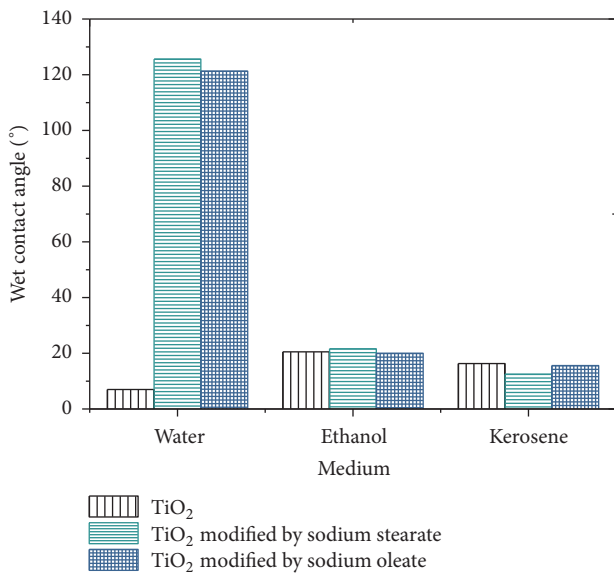


FIGURE 3: Change of wet contact angle of TiO_2 .

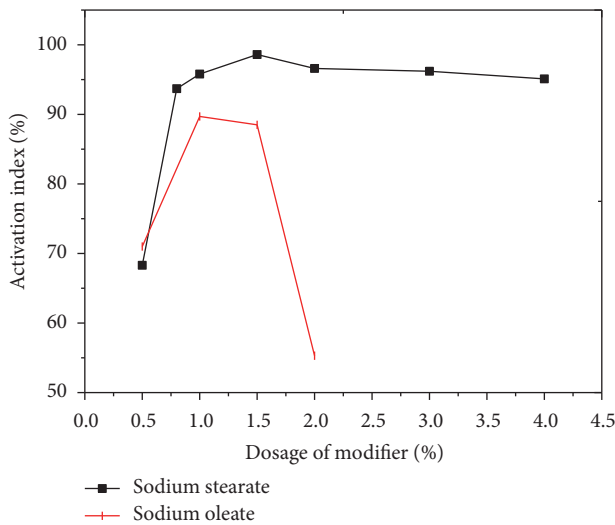
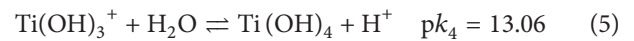
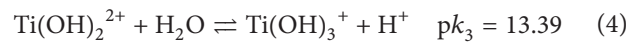
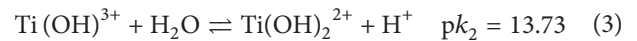
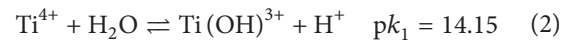


FIGURE 4: Activation index of modified TiO_2 with the amount of modifier.

of absorption peaks at 1557 cm^{-1} and 1470 cm^{-1} in the infrared spectrum of sodium stearate. It means that the chemical environment of C=O and -COO^- had significant change after sodium stearate reacted with TiO_2 . This may result from the chemical action between functional group of sodium stearate and surface functional group of TiO_2 (the hydroxide radical produced in Ti or Ti hydrolysis). Therefore, it is believed that the attachment of sodium stearate to TiO_2 particle surface has chemical properties. Sodium stearate is closely and firmly combined with TiO_2 particle, so the changes in surface characteristics of TiO_2 for modification are stable.

As shown in Figure 6, the infrared spectral features of TiO_2 modified with sodium oleate are similar to those of TiO_2 modified with sodium stearate. In the infrared spectroscopy of modified TiO_2 , there are characteristic absorption peaks representing methylene and methyl at 2852 cm^{-1} and 2922 cm^{-1} . This means that sodium oleate has attached to TiO_2 surface. The absorption peak at 1465 cm^{-1} indicates that chemical action occurred between -COO^- and TiO_2 in sodium oleate. Therefore, sodium oleate is also closely combined with TiO_2 particle for stable modification of TiO_2 .

3.3.2. Functional Group Morphology of TiO_2 Particle Surface in Water Medium. TiO_2 is one of the most typical oxides of surface hydroxylation, while the surface hydroxylation of TiO_2 as the semiconductor material is complex with various hydroxyl groups. Perrin made quantitative analysis on hydration reaction of titanium ion (Ti^{4+}) in water medium. The hydration reactions of Ti^{4+} in different levels and constants are as follows [32]:



$$pK_1 = \log \frac{[\text{Ti}(\text{OH})^{3+}][\text{H}^+]}{[\text{Ti}^{4+}]} \quad (6)$$

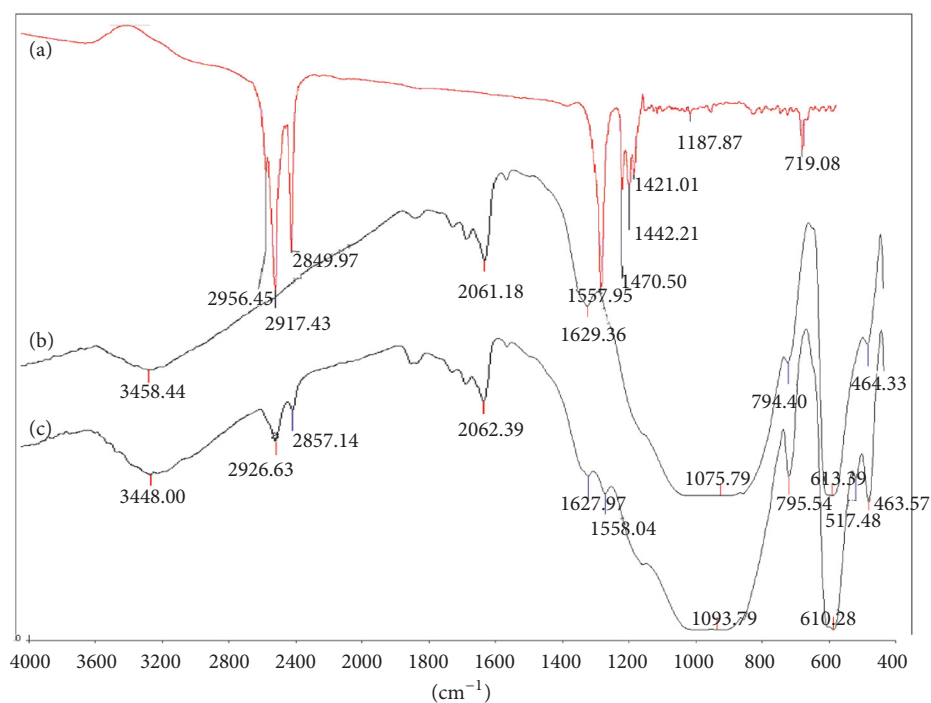


FIGURE 5: IR of TiO₂ modified by sodium stearate. (a) Sodium stearate; (b) TiO₂; (c) modified TiO₂.

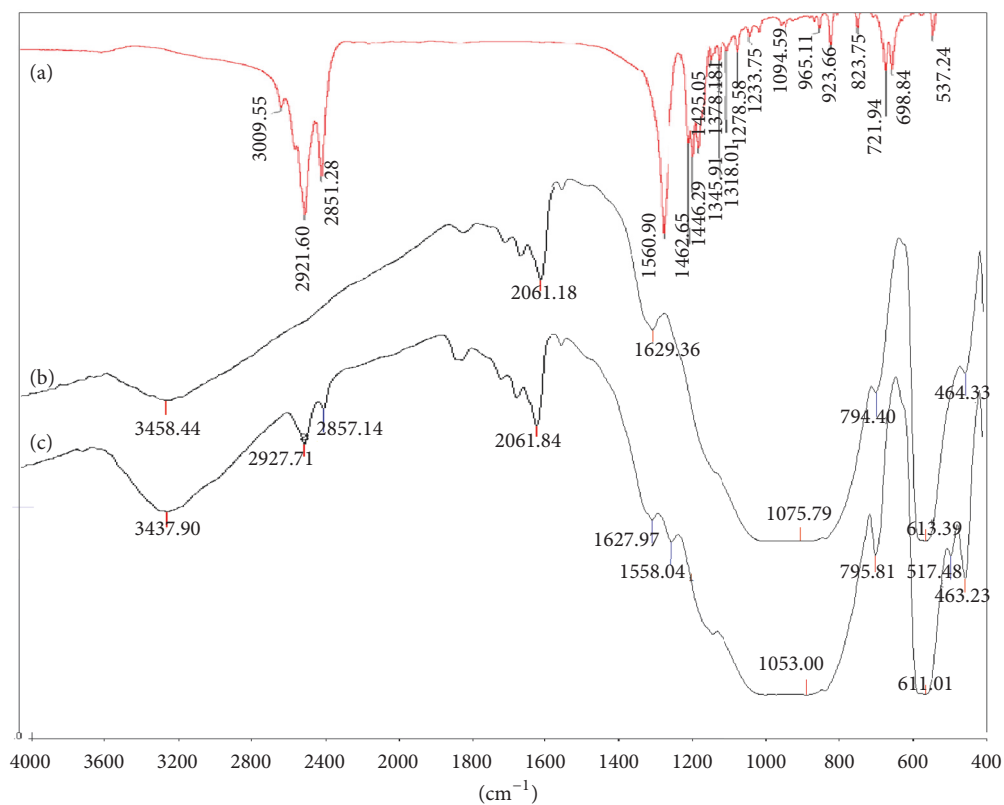


FIGURE 6: IR of TiO₂ modified by sodium oleate. (a) Sodium oleate; (b) TiO₂; (c) modified TiO₂.

$$pk_2 = \log \frac{[\text{Ti}(\text{OH})_2^{2+}][\text{H}^+]}{[\text{Ti}(\text{OH})_3^+]} \quad (7)$$

$$pk_3 = \log \frac{[\text{Ti}(\text{OH})_3^+][\text{H}^+]}{[\text{Ti}(\text{OH})_4]} \quad (8)$$

$$pk_4 = \log \frac{[\text{Ti}(\text{OH})_4][\text{H}^+]}{[\text{Ti}(\text{OH})_3^+]} \quad (9)$$

Therefore, the relationship between components, Ti^{4+} , $\text{Ti}(\text{OH})_3^+$, $\text{Ti}(\text{OH})_2^{2+}$, $\text{Ti}(\text{OH})_3^+$, and $\text{Ti}(\text{OH})_4$, and pH value ($-\log[\text{H}^+]$) is shown in Figure 7 [32].

Figure 7 shows that with the increase of pH value in system, Ti^{4+} tends to generate polyhydroxy. When $\text{pH} < 1$, $\text{Ti}(\text{OH})_2^{2+}$ is taken as the principal; when $\text{pH} = 2$, $\text{Ti}(\text{OH})_3^+$ is taken as the principal; when $\text{pH} > 4$, Ti^{4+} will turn to $\text{Ti}(\text{OH})_4$ component. The result also shows that even when $\text{pH} = 0 \sim 1$, the concentration of OH^- in system is extremely small. If the external action of hydrolysis is weak, no Ti^{4+} and $\text{Ti}(\text{OH})_3^+$ component is represented, meaning that the capability of Ti^{4+} is strong in generating various hydroxylates. It is obvious because the constants ($pk_1 \sim pk_4$) of Ti^{4+} hydrolysis reaction in different levels keep in very high value (13.06~14.15).

The hydroxylation characteristic of unsaturated Ti on TiO_2 surface can be deduced according to the hydrolysis behavior of Ti^{4+} . In other words, Ti is covered by a large amount of hydroxyl, so surface functional groups of TiO_2 are mainly OH-group as shown in Figure 8 [33]. This is similar with the molecule model of TiO_2 with surface attached with water proposed by Huaxiang and Xuxu [33].

3.3.3. Dissociation Morphology of Sodium Stearate and Sodium Oleate in Water Solution. The molecular formula of sodium stearate is $\text{CH}_3(\text{CH}_2)_{16}\text{COONa}$, while that of sodium oleate is $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COONa}$ (R-COONa for short). Both of them are composed of long chain of polar hydrophilic carboxyl and nonpolar hydrophobic alkane. They can dissolve in water solution, and then the dissolved components are rehydrated. The reaction formula is as follows:



Dianzuo and Yuehua [34] studied the relationship between the concentration of R-COO and R-COOH in sodium oleate solution and pH value (see Figure 9) [34]. The figure shows that the main morphology of R-COONa is R-COOH in the modification condition of TiO_2 , and only few R-COONa have coexistence of R-COOH and R-COO^- in this work. Therefore, it is believed that the action groups of TiO_2 modified with sodium stearate and sodium oleate are mainly R-COOH , followed by R-COO^- .

3.3.4. Model of Action between Modifier and TiO_2 Surface. The modification mechanism of sodium stearate and sodium oleate can be obtained according to above analysis on surface functional groups of TiO_2 particle and the dissociation

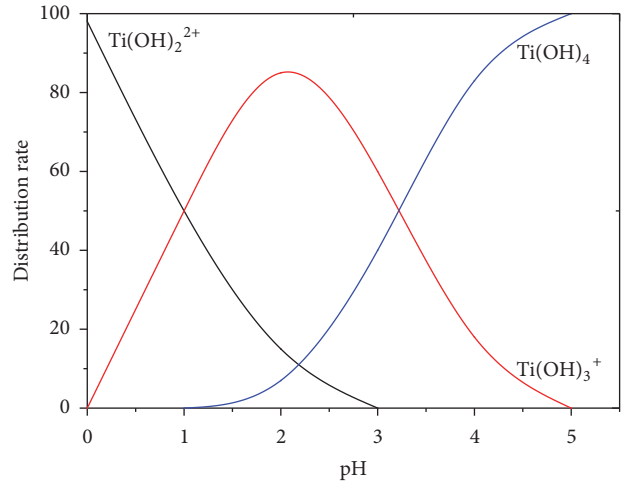


FIGURE 7: Distribution of Ti^{4+} hydrolysis component with pH value.

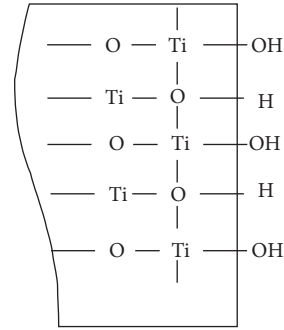


FIGURE 8: Schematic diagram of TiO_2 surface adsorbed hydroxyl.

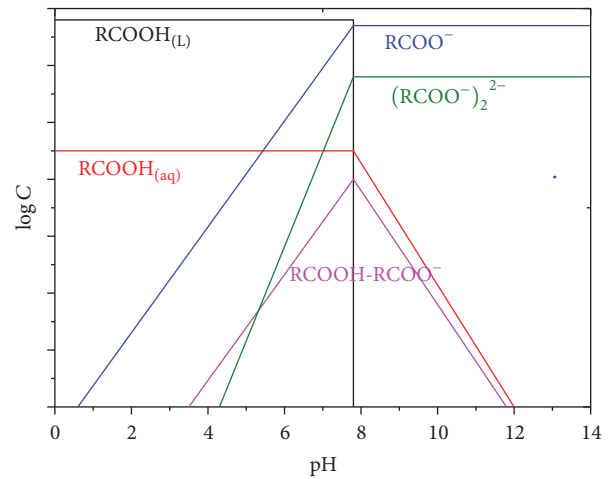


FIGURE 9: Distribution of sodium oleic acid in aqueous solution.

morphology of modifiers. Firstly, R-COOH forms a hydrogen bond with OH^- on TiO_2 particle surface for combination by dihydroxylation reaction. The combination can be realized by forming hydrogen bond with C=O and OH^- on TiO_2 surface through R-COO^- . Therefore, the modifier, R-COONa firmly attaches to TiO_2 particle surface to make organic

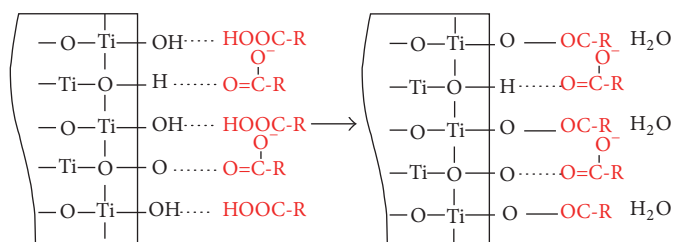


FIGURE 10: Schematic diagram of TiO_2 modified by sodium stearate and sodium oleate.

hydrocarbon chain distribute externally on particle surface. Therefore, TiO_2 has strong hydrophobicity. OH^- on TiO_2 surface is covered by R-COOH and R-COO^- attachment, so the absorption peaks reflect hydroxyl in infrared spectroscopy of TiO_2 after modification.

The reaction model of modifier on TiO_2 particle surface in wet process is established as according to above result analysis (See Figure 10).

4. Conclusions

Surface modification was conducted to TiO_2 particle with sodium stearate and sodium oleate. TiO_2 particle surface turns from hydrophilia to hydrophobicity, while the hydrophobicity degree can be controlled by changing modifier dosage.

In aqueous medium, wetting contact angle of TiO_2 particle greatly enlarges after modifying sodium stearate and sodium oleate. The increase of activation index shows that wettability in water medium becomes poor. The wetting contact angle of modified TiO_2 particle in absolute ethyl alcohol and kerosene is significantly lower than that in water medium, showing the good compatibility of organic matrix.

TiO_2 infrared spectroscopic analysis before and after modification shows that the modifier forms effective attachment on TiO_2 particle surface. With such attachment, inductive hydrophobicity forms on TiO_2 particle surface. It is relatively stable because attachment of modifier has certain chemical properties. The action model of TiO_2 modified with sodium stearate and sodium oleate was established based on the analysis on the functional groups of TiO_2 particle surface and the dissociation morphology of modifiers.

Disclosure

Zhou Hong is the first author.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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