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# Modification Strategies of Titanium Dioxide

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## Abstract

Titanium dioxide ( $\text{TiO}_2$ ) is a standard white pigment. However, when  $\text{TiO}_2$  is exposed to ultraviolet light, it will catalyze the degradation of the surrounding organic matrix. Surface coating of  $\text{TiO}_2$  is an effective method for reducing the catalytic effect of  $\text{TiO}_2$ . It can also improve the dispersion of  $\text{TiO}_2$  in an organic matrix. This review critically introduces recent results on the surface coating of  $\text{TiO}_2$ . First, the main features of  $\text{TiO}_2$ , including processes, structure, and final properties, are described briefly. Second, this chapter reports and discusses different surface coating methods for  $\text{TiO}_2$  with inorganic oxides and organic matter. Inorganic oxides, such as  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ , and  $\text{ZrO}_2$ , would form a continuous dense film and block the defects of the  $\text{TiO}_2$  lattice. They can give  $\text{TiO}_2$  excellent weather resistance. The organic matter available for surface treatment includes the surfactant, the coupling agent, and the macromolecule. They can improve the affinity of  $\text{TiO}_2$  with various organic matrices. Surfactant treatment is relatively simple. Coupling agents can give  $\text{TiO}_2$  more novel properties, such as thermal stability. Macromolecules can increase the volume of  $\text{TiO}_2$  particles through steric hindrance and improve the dispersion of  $\text{TiO}_2$  in an organic matrix. However, coating  $\text{TiO}_2$  in a single matter is challenging to meet the increasing performance requirements. Therefore, it is necessary to study further the effect of co-coating with different inorganic oxides and organic matter on the structure and properties of  $\text{TiO}_2$ .

**Keywords:** titanium dioxide, inorganic coating, organic coating, structure, pigmentary properties

## 1. Introduction

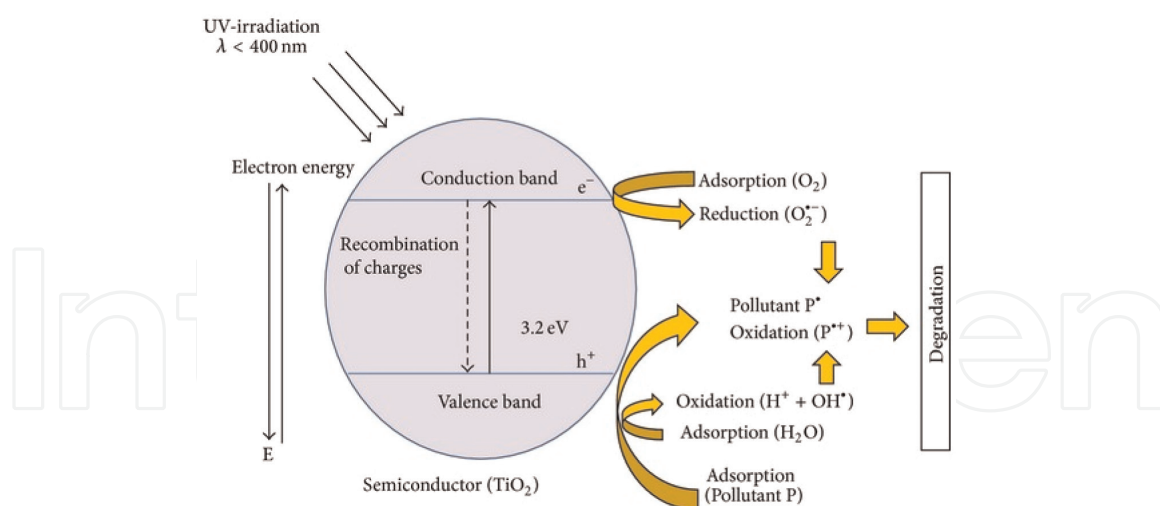
Since the discovery of titanium in 1791,  $\text{TiO}_2$  has been used commercially for over 100 years. Compared with other white pigments, such as  $\text{ZnS}$ ,  $\text{BaSO}_4$ ,  $\text{ZnO}$ , etc.,  $\text{TiO}_2$  is a nontoxic, stable pigment [1]. It shows high hiding power, refractive index, whiteness, and other excellent physical properties (**Table 1**) [2]. As a result,  $\text{TiO}_2$  is widely used in printing ink, plastics, paper, coating materials, and cosmetics. It is also an indispensable raw material for the light industry, electronic industry, and other fields [3].  $\text{TiO}_2$  is produced by the sulfate and chloride process. The quality of  $\text{TiO}_2$  produced by the two processes is different (**Table 2**) [2, 4]. Upmarket  $\text{TiO}_2$  is mainly produced by the chloride process [5].

Pigment	Relative density	Refractive index	Lightening power		Covering power/%
			Reynolds number	Relative value/%	
Rutile TiO <sub>2</sub>	4.20	2.76	1650	100	100
Anatase TiO <sub>2</sub>	3.91	2.55	1270	77	78
ZnS	4.00	2.37	660	40	39
BaSO <sub>4</sub>	4.50	1.64	—	—	—
Sb <sub>2</sub> O <sub>3</sub>	5.67	2.09	280	17	15
ZnO	5.60	2.02	200	12	14
Lithopone	4.20	1.84	260	16	—
Lead white (basic lead carbonate)	6.10	2.00	159	9	12

**Table 1.**  
Technical index comparison of white pigment [2].

	Sulfate process	Chloride process
Raw ore	(1) Titanium concentrate: low price, stable, can be obtained directly from mining; (2) acid-soluble titanium slag: relatively high price, good quality, need to be chemically processed	(1) Titanium concentrate/white titanium: low price, stable, high process technology requirements; (2) rutile: relatively high price, low process technology requirements; (3) Titanium chloride slag and artificial rutile: higher price, low process technology
Auxiliary raw materials	H <sub>2</sub> SO <sub>4</sub>	Cl <sub>2</sub>
Price	Low	High
Type	Anatase, middle-end rutile	High-end rutile
H <sub>2</sub> SO <sub>4</sub> recovery/%	13	75
Flow	Long and complex	Short and simple process
Technology	Mature	Domestic immaturity
Control accuracy	Low	High
Quality	Coverage and yellowing resistance are weaker than chloride methods but cheaper and less used in specific areas such as papermaking and chemical fiber	High purity, good comprehensive performance, high price
Energy consumption	(1) Pressure on environmental protection, but recycling of waste by-products can be improved; (2) large consumption of coal, natural gas, steam, water, and electricity	(1) Less three wastes, small pressure for environmental protection, but the treatment of ferric chloride in solid waste is difficult; (2) consumption is relatively small
Government policy	Restricted	Supported

**Table 2.**  
Comparison of different processes [2, 4].



**Figure 1.**  
The main photocatalytic process of  $\text{TiO}_2$  [9].

$\text{TiO}_2$  shows a regular lattice structure. There are three crystalline forms of  $\text{TiO}_2$  in nature: anatase, rutile, and brookite [6]. Anatase has a tetragonal crystal system. However, it will slowly transform into rutile after heating at about  $610^\circ\text{C}$  [7] and completely transform into rutile at  $915^\circ\text{C}$ . The latter also has a tetragonal crystal structure, each unit contains six atoms, and its oxygen atoms are densely packed, so rutile shows the highest stability [8]. Compared with anatase, rutile exhibits higher density, hardness, refractive index, and dielectric constant.

$\text{TiO}_2$  has excellent physical and chemical properties, however,  $\text{TiO}_2$  surface has a photocatalytic active site (**Figure 1**). After absorbing ultraviolet light energy, electron-hole pairs (the charge carrier) are generated [10]. The valence band hole ( $h^+$ ) is highly oxidizing while the conduction band electron ( $e^-$ ) is highly reducing [11]. The  $h^+$  oxidizes  $\text{H}_2\text{O}$  or  $\text{OH}^-$  ion to the hydroxyl radical ( $\text{OH}^\bullet$ ), the  $e^-$  reduces adsorbed oxygen ( $\text{O}_2$ ) species to superoxide ( $\text{O}_2^{\bullet-}$ ) and then undergoes a series of reactions to give the  $\text{OH}^\bullet$  radical. These radicals will react with surrounding organic substances, resulting in the decomposition of the organic matrix [12]. What's worse,  $\text{TiO}_2$  particles are easy to agglomerate due to the high special surface area, causing poor dispersion in the organic matrix [13].

To overcome the drawbacks of  $\text{TiO}_2$  mentioned above, one can use coatings. The coating of  $\text{TiO}_2$  by inorganic oxides, such as alumina, silica, and zirconia [14], can effectively inhibit the oxidative degradation of the organic matrix, finally improving the light and weather resistance [15, 16]. The poor dispersion of  $\text{TiO}_2$  can also be effectively solved by coating [17]. Therefore, it is of great social significance and economic value to study the coating of  $\text{TiO}_2$  to improve the physical stability and dispersion, extending new applications of  $\text{TiO}_2$ . In this chapter, we introduce the modification strategies of  $\text{TiO}_2$  to the readers. To fully describe the modification mechanism, processes and properties of modified  $\text{TiO}_2$  will be discussed.

## 2. Inorganic modification of $\text{TiO}_2$

The purpose of the inorganic modification is to coat  $\text{TiO}_2$  with a layer of the inorganic hydrated oxide film. This film can block and cover the lattice defects of  $\text{TiO}_2$  and reduce the connecting possibility between organic matrix and active groups of  $\text{TiO}_2$ . Such films comprise alumina, silica, zirconia, etc.

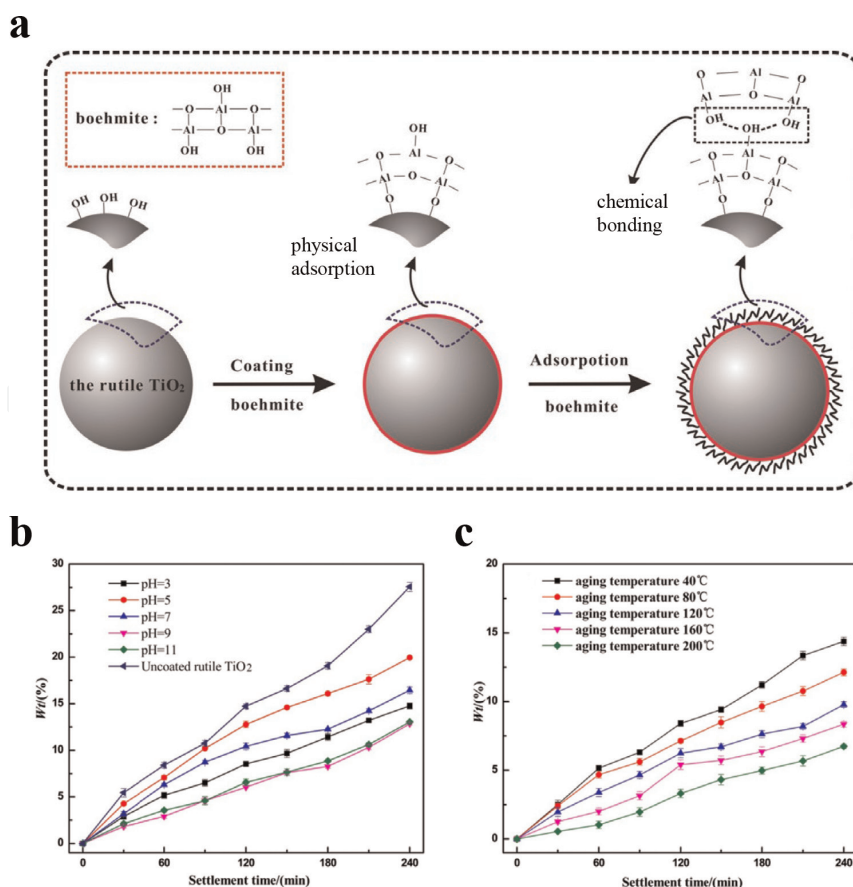
## 2.1 Alumina

Alumina ( $\text{Al}_2\text{O}_3$ ) is a suitable electron acceptor, which can annihilate the photo-electrons generated by  $\text{TiO}_2$  after ultraviolet absorption and excitation, inhibiting subsequent active groups' generation [18]. In addition,  $\text{Al}_2\text{O}_3$  can also reflect ultraviolet from natural light [19]. Thus,  $\text{Al}_2\text{O}_3$  is one of the most used materials for the inorganic coating of  $\text{TiO}_2$ .

A variety of chemicals, such as sodium metaaluminate ( $\text{NaAlO}_2$ ) and aluminum sulfate ( $\text{Al}_2(\text{SO}_4)_3$ ), have been used for  $\text{TiO}_2$  coating. These metal salts are added into  $\text{TiO}_2$  suspension at various pH, and the positively charged OH-Al hydrolyzed by soluble salt is adsorbed and wrapped on the surface of  $\text{TiO}_2$  particles to form hydrated alumina. The structure of hydrated alumina will change at different pH values. It shows an amorphous structure at pH 5, a floccular false boehmite structure at pH 8–10, and a flaky gibbsite structure at pH above 10.

Zhang et al. [20] reported the preparation of compact amorphous  $\text{Al}_2\text{O}_3$  film on the  $\text{TiO}_2$  under the molar ratio  $\text{NaAlO}_2/\text{TiO}_2$  of 1/22 at  $80^\circ\text{C}$  in pH 5. After being coated by  $\text{Al}_2\text{O}_3$  films, the whiteness and brightness of the modified  $\text{TiO}_2$  samples increased with the increase of the  $\text{Al}_2\text{O}_3$  loading, while the relative light scattering index depended on the alumina loading.

Dong et al. [21] synthesized alumina-coated rutile  $\text{TiO}_2$  samples using the chemical liquid deposition method under various pH and aging temperatures. The results showed that this film-coating process should mainly be attributed to chemical bonding and physical adsorption (Figure 2a). The higher aging temperature was in favor of



**Figure 2.** (a) Schematic diagram of physical adsorption and chemical bonding of  $\text{Al}_2\text{O}_3$  coated rutile; dispersion stability of  $\text{Al}_2\text{O}_3$ -coated rutile  $\text{TiO}_2$  samples at different pH values (b) and aging temperatures (c) [21].

the elevation of the boehmite content of the coating film, causing the enhancement of dispersion stability. It contributed to the increase of steric hindrance and electrostatic repulsion. The coated TiO<sub>2</sub> exhibited well dispersion stability at pH 9 (**Figure 2b**) and aging temperature 200°C (**Figure 2c**), respectively.

Wu et al. [22] discussed the mechanism of the film-coating process of hydrated alumina on TiO<sub>2</sub> particles in an aqueous solution. The effects of temperature, pH value, and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solution were investigated. It is found that TiO<sub>2</sub> particles promote the hydrolysis of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> in both acidic and basic solutions and adsorb positively charged OH-Al species in slurries. When the OH-Al species or TiO<sub>2</sub> particles have enough energy to cross the repulsion threshold, the hydroxyl groups on the surface of the TiO<sub>2</sub> particles will condense with the OH-Al species, leading to the coating of OH-Al species on the surface of the TiO<sub>2</sub> particles. As a result, the Al<sub>2</sub>O<sub>3</sub> film is formed.

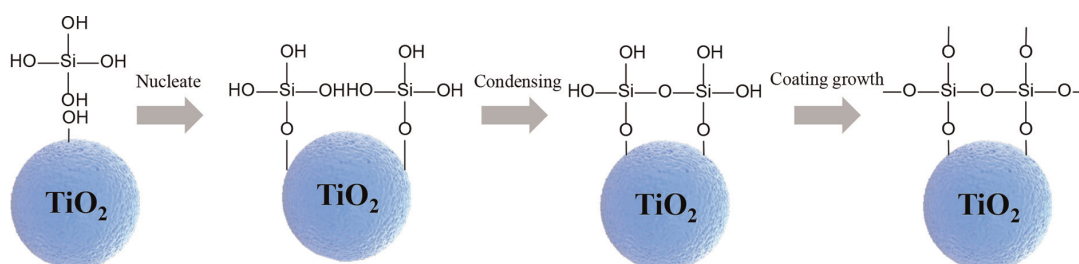
## 2.2 Silica

Silica coating shows a similar function as alumina. Compared with alumina, silica film gives more chemical stability to TiO<sub>2</sub>. TiO<sub>2</sub> suspension is added to water-soluble silicon compound in base condition. Silicon is deposited on TiO<sub>2</sub> particles as Si(OH)<sub>4</sub> through physical adsorption and chemical bonding between Si(OH)<sub>4</sub> and TiO<sub>2</sub>. The deposited Si(OH)<sub>4</sub> is further condensed into a silica gel, finally realizing the coating of TiO<sub>2</sub> particles (**Figure 3**).

Liu et al. [23] prepared SiO<sub>2</sub>-coated TiO<sub>2</sub> powders by the chemical deposition method starting from rutile TiO<sub>2</sub> and Na<sub>2</sub>SiO<sub>3</sub>. The evolution of island-like and uniform coating layers depended on the ratio of Na<sub>2</sub>SiO<sub>3</sub> to TiO<sub>2</sub>, reaction temperature, and pH. The result showed that the whiteness and brightness of the TiO<sub>2</sub> product increased with the loading of SiO<sub>2</sub>.

Lin et al. [24] studied the surface characteristics of hydrous silica-coated TiO<sub>2</sub> particles. Different analytical techniques were used to characterize the silica oxide coatings on TiO<sub>2</sub> particles. Analyses showed that hydrous silica is continuously coated on the surface of TiO<sub>2</sub> particles. The hydrous silica film coating can improve the durability of pigment weather and dispersion properties.

SiO<sub>2</sub> can be easily deposited on TiO<sub>2</sub> surfaces. However, SiO<sub>2</sub> coating layers with a lower polarity cannot significantly enhance the dispersibility of TiO<sub>2</sub> in a polar solvent. Moreover, the hydrogen bond interaction between the hydrated SiO<sub>2</sub> will lead to thixotropy. Al<sub>2</sub>O<sub>3</sub> coating layers with many –OH groups not only improve the dispersibility of TiO<sub>2</sub> powders in polar solvents but also provide abundant active sites for further organic modification. However, Al<sub>2</sub>O<sub>3</sub> coating layers tend to anchor loosely at TiO<sub>2</sub> surfaces. Therefore, various reports are about the formation of binary Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> films on the TiO<sub>2</sub> surface.



**Figure 3.**  
Scheme of silica coating process.

Zhang et al. [25] prepared binary  $\text{Al}_2\text{O}_3/\text{SiO}_2$ -coated rutile  $\text{TiO}_2$  composites by a liquid-phase deposition method starting from  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$  and  $\text{NaAlO}_2$ . The formation of continuous and dense binary  $\text{Al}_2\text{O}_3/\text{SiO}_2$  coating layers depended on the pH value of the reaction solution and the alumina loading. The coated  $\text{TiO}_2$  particle had a high dispersibility in water. Compared with  $\text{SiO}_2$ -coated  $\text{TiO}_2$  samples, the whiteness and brightness of the binary  $\text{Al}_2\text{O}_3/\text{SiO}_2$ -coated  $\text{TiO}_2$  particles were higher.

To improve the dispersion and reduce the photocatalytic activity of  $\text{TiO}_2$ , Godnjavec et al. [26] modified  $\text{TiO}_2$  by the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  films on the surface of particles and incorporated modified  $\text{TiO}_2$  into the polyacrylic coating. The results showed that surface treatment of  $\text{TiO}_2$  with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  could improve the dispersion of  $\text{TiO}_2$  in the polyacrylic matrix, and the UV protection of the clear polyacrylic composite coating was enhanced.

### 2.3 Zirconia

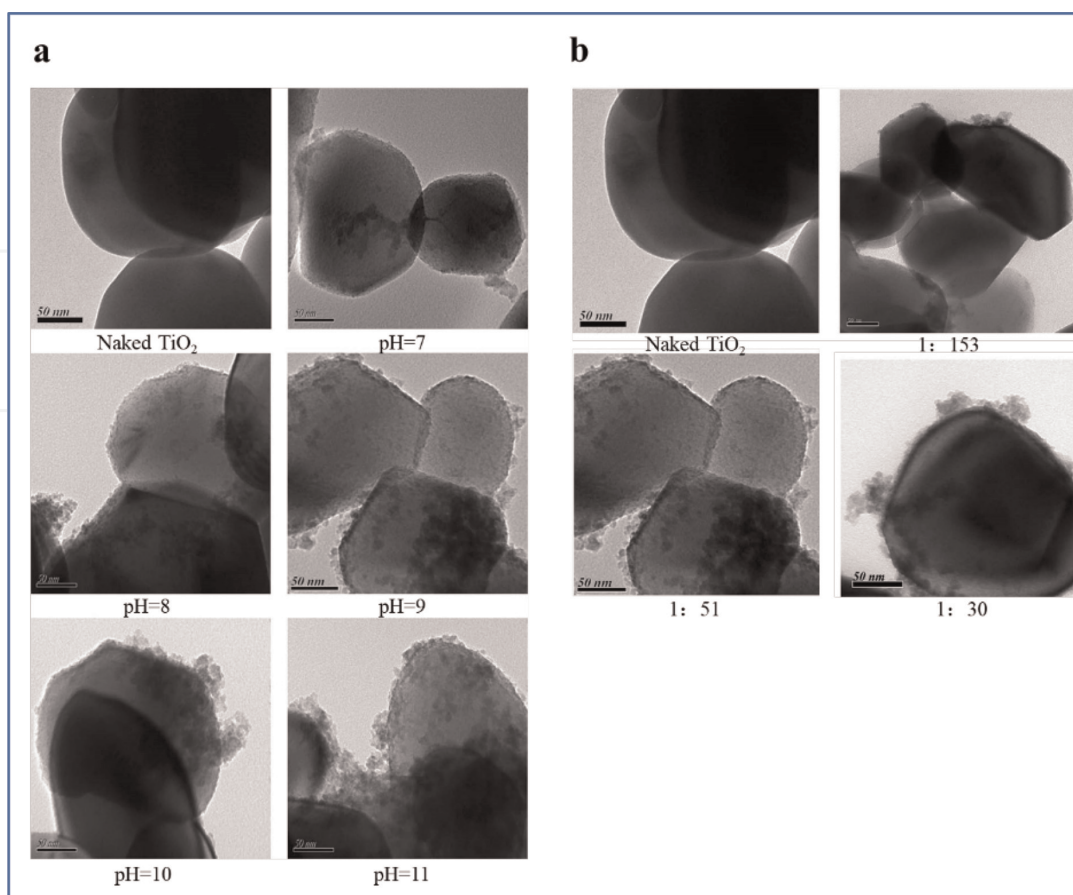
Zirconia ( $\text{ZrO}_2$ ) has a high refractive index (2.170) and weak ultraviolet light absorption. Therefore, the  $\text{ZrO}_2$  coating considerably reduces UV absorption causing higher photostability [27] and increasing the glossiness of  $\text{TiO}_2$  particles. This coating can increase the amount of hydroxyl groups on the surfaces of the  $\text{TiO}_2$  particles, which improves the dispersibility of  $\text{TiO}_2$  powders in aqueous media and provides more active sites for the subsequent organic modification.

The  $\text{TiO}_2$  powders are dispersed in distilled water with ultrasonic treatment to obtain  $\text{TiO}_2$  suspension, and the zirconium salt solution is added as follows. The zirconium salt hydrolyzes rapidly, and the zirconia nanoparticles grow and form aggregates on the surface of  $\text{TiO}_2$  through  $\text{Zr-O-Ti}$  bonds. The zirconia nanoparticles will grow and form a continuous and dense film.

Zhang et al. [28] reported that the  $\text{ZrO}_2$ -coated rutile  $\text{TiO}_2$  could be prepared by the chemical liquid deposition method starting from rutile  $\text{TiO}_2$  and  $\text{ZrOCl}_2$ . The formation of zirconia coating depended on pH value of reaction solution and the mole ratio of  $\text{ZrOCl}_2$  to  $\text{TiO}_2$ . When the pH value reached to 9 with a mole ratio of  $\text{ZrOCl}_2$  to  $\text{TiO}_2$  of 1:51, the zirconia aggregates with an average particle size of about 4 nm coated on the surface of the  $\text{TiO}_2$  particles (**Figure 4a, b**). Compared with the exposed rutile  $\text{TiO}_2$ , the dispersibility, whiteness, brightness, and relative light scattering index of the  $\text{ZrO}_2$ -coated  $\text{TiO}_2$  were significantly improved.

Li et al. [29] prepared  $\text{ZrO}_2$ -coated  $\text{TiO}_2$  by a precipitation method. The  $\text{Zr}(\text{SO}_4)_2$  solution was added to  $\text{TiO}_2$  suspension at the pH of 5.2 at  $50^\circ\text{C}$ . The mass ratio of  $\text{ZrO}_2$  to  $\text{TiO}_2$  was 1.0%, and a dilute  $\text{NaOH}$  solution was used to adjust the pH value. The results showed that supersaturation of the  $\text{Zr}(\text{SO}_4)_2$  solution is one of the key factors influencing the type of nucleation in the zirconia coating. Lower supersaturation benefits the heterogeneous nucleation of zirconia on the surface of  $\text{TiO}_2$  particles, while higher supersaturation leads to the homogeneous nucleation of zirconia itself. A suitable  $\text{ZrO}_2$  content is about 1.0 wt.%, and this thick and continuous film gives better pigmentary properties.

To sum up, the function of the inorganic oxide-coated film of  $\text{TiO}_2$  is to form a barrier, reducing the photoactivity of  $\text{TiO}_2$  and the production of free radicals on the surface of  $\text{TiO}_2$ . As a result, the coated  $\text{TiO}_2$  has good pigmentary properties, including weather and light resistance. However, using a single inorganic oxide coating is often not sufficient to meet the requirements of several applications. So, it is one of the



**Figure 4.** TEM micrographs of bare rutile TiO<sub>2</sub> and ZrO-coated TiO<sub>2</sub> at  $T = 80^{\circ}\text{C}$ ,  $\text{ZrOCl}_2:\text{TiO}_2 = 1:51$  with different pH (a) and with a different molar ratio of  $\text{ZrOCl}_2$  to  $\text{TiO}_2$  (b) [28].

essential directions to study further the co-coating of various inorganic oxides and the regulation and process of coating structure.

### 3. Organic modification of TiO<sub>2</sub>

Modifying TiO<sub>2</sub> by organic agents is realized by coating them with organic substances such as surfactants, coupling agents and polymers. It can improve the affinity of TiO<sub>2</sub> particles with organic matrices, resulting in better dispersion of TiO<sub>2</sub>. Thus, the pigmentary properties of TiO<sub>2</sub>, such as tint-reducing power, hiding power, and whiteness, are shown.

In the modification, there are two mechanisms: physical adsorption of organic agents on the surface of TiO<sub>2</sub> and chemical bonding between TiO<sub>2</sub> and organic agents [30]. The principle of physical adsorption is that the hydrophilic group of the organic coating agent is adsorbed on the surface of TiO<sub>2</sub> particles. In contrast, the oleophilic group is outwardly affinity to the surrounding polymer matrix. Therefore, the polymer chains can penetrate the TiO<sub>2</sub> aggregates and separate the TiO<sub>2</sub> particles, finally improving the dispersion of TiO<sub>2</sub>. For chemical bonding, the hydroxyl groups on the surface of TiO<sub>2</sub> particles act as active sites, which will react with organic coating agents and form covalent bonds. As a result, the TiO<sub>2</sub> particles change from hydrophilic to hydrophobic. Several kinds of organic agents can be used for the surface modification of TiO<sub>2</sub>, including surfactants, coupling agents and polymers.



### 3.1 Surfactants

Surfactants can be divided into cationic, anionic, and nonionic surfactants. One can use surfactants singly or together to modify TiO<sub>2</sub> particles to evaluate the performance of TiO<sub>2</sub>. Li et al. [31] chose anionic sodium dodecyl sulfate (SDS) and nonionic nonylphenol ethoxylate (NPEO, Tergitol NP-9) to study the effect of surfactants on the behaviors of TiO<sub>2</sub> in aqueous solution. The results showed that both surfactants could be adsorbed onto the surface of nano-TiO<sub>2</sub> but that only SDS can significantly decrease the zeta potential of TiO<sub>2</sub>. Both surfactants reduced the aggregation of TiO<sub>2</sub> and retarded the aggregate sedimentation at surfactant concentrations  $\geq 0.015\%$  (w:v). In addition, SDS exerted a more substantial reductive effect than NP-9.

Wei et al. [32] used different surfactants, such as cetyltrimethylammonium bromide (CTAB), sodium dodecylbenzene sulfonate (SDBS), and diethanolamine (DEA), to modify TiO<sub>2</sub> particles. The crystal type of TiO<sub>2</sub> has no noticeable change with the addition of different surfactants, but the morphology, size, and dispersion of the TiO<sub>2</sub> particles have changed to some extent. Among the three surfactants, CTAB is beneficial in reducing TiO<sub>2</sub> particle size and improving TiO<sub>2</sub> dispersion and agglomeration. And this CTAB-coated TiO<sub>2</sub> had the greatest photostability in methyl orange degradation.

Wittmar et al. [33] prepared modified TiO<sub>2</sub> particles by adding a cationic imidazolium salt solution. It was found that an increase in the alkyl chain length was beneficial, leading to a narrowing of the particle size distribution and a decrease of the agglomerate size in dispersion. The smallest average nanoparticle sizes in dispersion were around 30 nm.

Zhang et al. [34] discussed the influence of different surfactants on the thermal stability, weather fastness, and pigmentary properties of TiO<sub>2</sub> particles. The results are collected in **Table 3**. Compared with neopentyl glycol (NPG),

Coating agent	Dosage /%	Hue			Oil absorption /%	290°C evaporation /%
		L (Whiteness)	a (Red and green saturation)	b (Blue and green saturation)		
TMP	0.3	97.64	-0.41	2.39	15.98	0.41
	0.5	97.64	-0.43	2.29	14.72	0.43
	0.7	97.18	-0.52	2.23	13.95	0.52
	0.9	96.85	-0.53	2.14	13.49	0.54
NPG	0.3	97.54	-0.40	2.46	16.26	0.49
	0.5	97.49	-0.46	2.29	16.01	0.52
	0.7	97.21	-0.53	2.9	15.69	0.56
	0.9	96.89	-0.56	2.10	15.33	0.60
PEG	0.3	97.59	-0.42	2.49	16.86	0.44
	0.5	97.53	-0.44	2.39	16.56	0.49
	0.7	97.26	-0.57	2.23	16.01	0.53
	0.9	7.00	-0.61	2.10	15.49	0.59

Coating agent	Dosage /%	Hue			Oil absorption /%	290°C evaporation /%
		L (Whiteness)	a (Red and green saturation)	b (Blue and green saturation)		
TME	0.3	97.62	-0.44	2.42	17.37	0.43
	0.5	97.59	-0.49	2.31	17.04	0.49
	0.7	97.35	-0.55	2.26	16.55	0.52
	0.9	96.92	-0.59	2.09	16.01	0.61
Raw TiO <sub>2</sub>	/	97.01	-0.50	2.22	14.29	0.44

**Table 3.**  
 Routine index of TiO<sub>2</sub> [34].

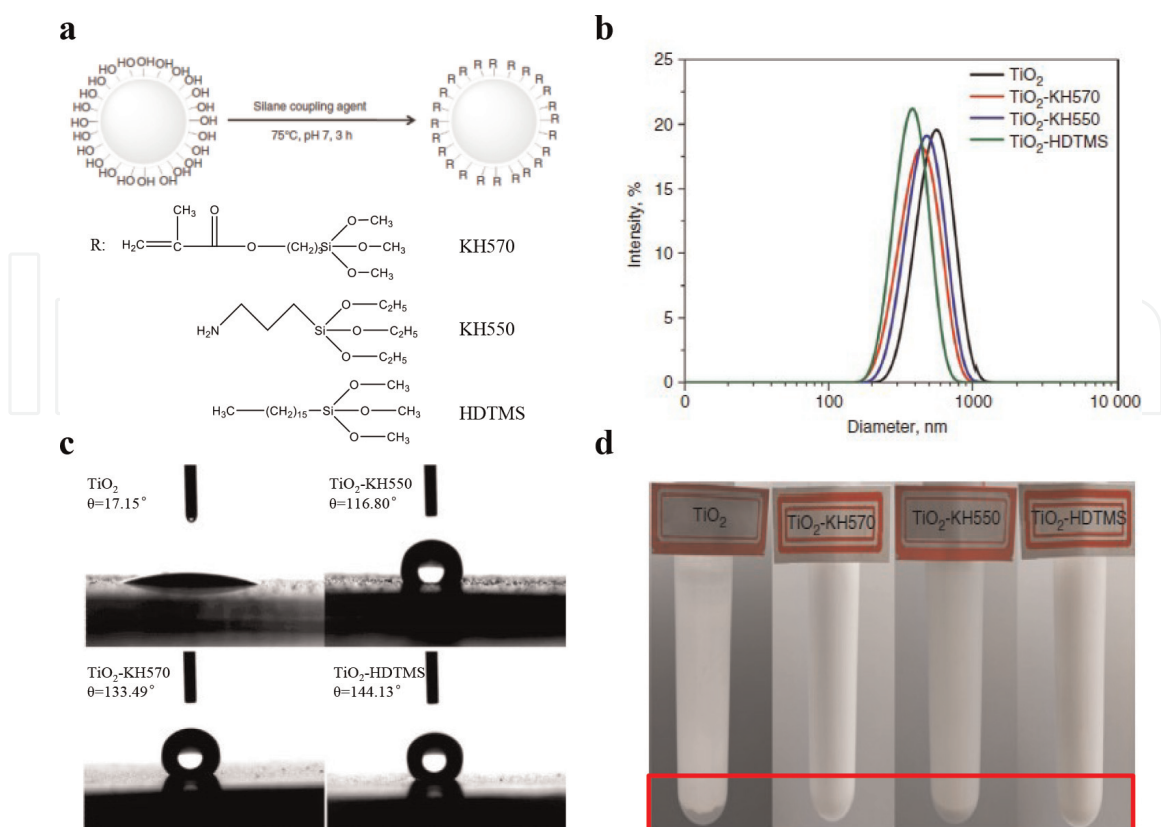
polyethylene glycol (PEG) and trimethylolethane (TME), trimethylolpropane (TMP) can bring the highest whiteness (97.64 of *L*) to TiO<sub>2</sub> particles only in the content of 0.3 wt%.

### 3.2 Coupling agent

Coupling agents are amphoteric structural compounds, which can be divided into silane coupling agents, titanate coupling agents, aluminate coupling agents, etc. One end group of the coupling agent can react with the hydroxyl group on the surface of TiO<sub>2</sub> particles to form a strong chemical bond. The other can react with the polymeric matrix. Consequently, two kinds of materials of different polarity, TiO<sub>2</sub>, and a polymer, are closely combined to give the composite material excellent comprehensive performance.

Silane coupling agents were first developed and used widely to modify TiO<sub>2</sub>. In the reaction, organic silicon is adsorbed on TiO<sub>2</sub>, and the molecule part reacts with the hydroxyl group on the surface of TiO<sub>2</sub> to prevent the aggregation of particles. Wang et al. [35] reported the modification of TiO<sub>2</sub> by three kinds of silane coupling agents (KH550, KH570, and HDTMS). The chemical structure and the reaction mechanism with TiO<sub>2</sub> are shown in **Figure 5(a)**. The results showed that TiO<sub>2</sub> modified by silane coupling agent had small particle size, improved hydrophobicity, and low surface energy (**Figure 5(b, c)**). Furthermore, compared with raw TiO<sub>2</sub> and KH550 coated TiO<sub>2</sub>, HDTMS-coated TiO<sub>2</sub> and KH 570 coated TiO<sub>2</sub> had excellent dispersion stability as white pigments in blue light curing inks (**Figure 5(d)**).

Sabzi et al. [36] used aminopropyl trimethoxyl silane (APS) as a coupling agent to modify TiO<sub>2</sub>. The results showed that silane coupling agents could significantly improve the dispersion of TiO<sub>2</sub> in polyurethane composite and the mechanical properties of composite. Xuan et al. [37] reported the modification of TiO<sub>2</sub> by vinyltrimethoxyl silane (A171) and the reinforcement of modified TiO<sub>2</sub> on wheat straw fiber/polypropylene composite. The modified TiO<sub>2</sub> could effectively improve the tensile, flexural, and impact resistance as well as the UV light stability of the composite. However, the thermal stability of the coupling agents is poor. This leads to the degradation of the organic layer on the surface of TiO<sub>2</sub>. Finally, the color and whiteness of TiO<sub>2</sub> are changed.



**Figure 5.** (a) The scheme of reaction between silane coupling agents with different chemical structures and TiO<sub>2</sub> particle, (b) particle size distribution of raw and modified TiO<sub>2</sub>, (c) contact angle of raw and modified TiO<sub>2</sub>-water interface, (d) dispersion of raw and modified TiO<sub>2</sub> [35].

### 3.3 Polymer

The above two organic treatment methods depend on the reaction of small molecular modifiers with the surface groups of TiO<sub>2</sub>. In contrast, a modification with a macromolecule uses the polymer to coat the TiO<sub>2</sub> particles directly or the reactive monomer to polymerize on the surface of TiO<sub>2</sub> particles. In the coating with polymers, there is no interaction between the polymeric groups and TiO<sub>2</sub>, but the polymer induces a steric hindrance [38]. As a result, the dispersion of TiO<sub>2</sub> in the subsequent polymer matrix is improved. TiO<sub>2</sub> shows good pigmentary properties. The reaction mechanism and classification of polymer coating modification are collected in **Table 4**.

Man et al. [40] used the microcapsule method to modify TiO<sub>2</sub>. The *in situ* polymerization of acrylic monomer on the surface of TiO<sub>2</sub> particles obtained the core-shell structure of modified TiO<sub>2</sub>. This core-shell structure TiO<sub>2</sub> showed improved dispersion in organic media and excellent UV shielding ability. Olad et al. [41] used polyaniline (PANI) to modify TiO<sub>2</sub> through *in situ* polymerization. The results showed that PANI was successfully implanted on the surface of TiO<sub>2</sub>, effectively inhibiting the aggregation of TiO<sub>2</sub> nanoparticles.

In the “Anchor positioning” coating method, the polymers used are named hyper-dispersant, which Schofield first proposed in the 1980s. Compared with the structure of traditional dispersants, such as surfactant SDS, with the hydrophilic and lipophile groups, hyper-dispersants have two completely different groups: anchoring group and

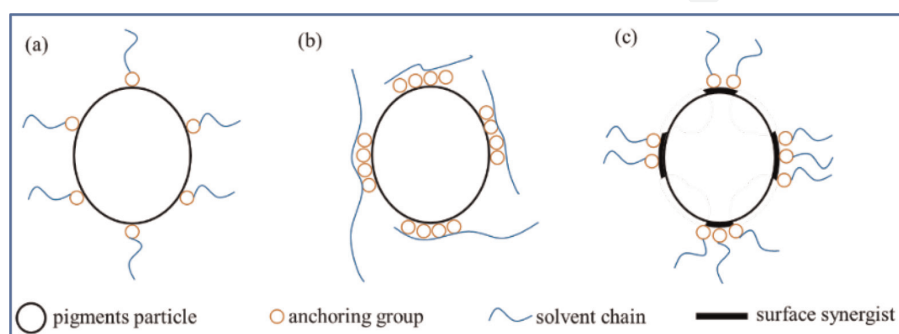
Method	Mechanism	Classification
Microcapsule method	The continuous and dense polymer capsule is formed by <i>in situ</i> polymerization with active monomer or adsorbing polymers directly using the Van der Waals force	<ol style="list-style-type: none"> <li>1. Active monomers are adsorbed on the surface of TiO<sub>2</sub> and then polymerized.</li> <li>2. Surface active points of TiO<sub>2</sub> are stimulated and initiate the polymerization of the monomer.</li> <li>3. Polymer chains are adsorbed directly to form a dense film on the surface of TiO<sub>2</sub> by using Van der Waals force</li> </ol>
Surface grafting modification	The surface of inorganic particles was pretreated first, and graft polymerization was initiated. There are two different pretreatments: coupling agent pretreatment and surfactant pretreatment	<ol style="list-style-type: none"> <li>1. Surface coupling reaction with polymerizable organic monomers.</li> <li>2. Introducing free radical-producing compounds to graft polymerizable organic monomers.</li> <li>3. The free radicals of the particle itself capture the polymer chain to achieve graft polymerization</li> </ol>
“Anchor positioning” coating	The functional group of the polymer can anchor on the surface of TiO <sub>2</sub> , and the solvent chain of the polymer extends in a nonaqueous system to provide steric stability	Terminal group anchoring method of macromolecules

**Table 4.**  
 Modification by polymer coating [39].

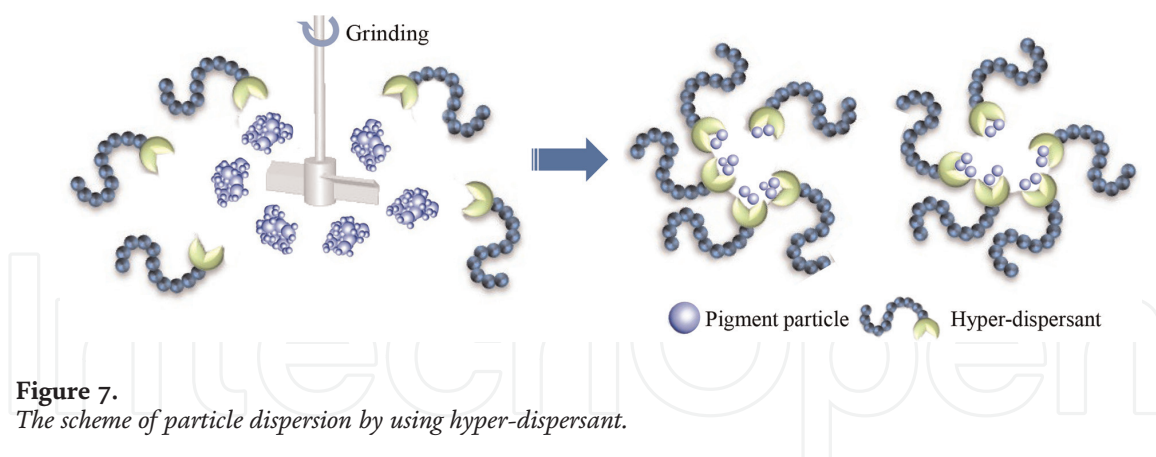
solvent group. The anchoring groups are anchored on the particles’ surface by single-point or multipoint anchoring or co-anchoring with a surface synergist (**Figure 6**). At the same time, the solvent chain is extended in a nonaqueous system to provide steric stability. Therefore, the particles are stably dispersed (**Figure 7**). So, the hyper-dispersants have a unique dispersion effect on the nonaqueous system.

There are a lot of different anchoring groups, and solvent chains can be designed to synthesize hyper-dispersant (**Tables 5 and 6**). Thus, hyper-dispersants with different effects can be designed and synthesized by selecting different anchoring groups and solvent chains.

Schaller et al. [43] modified TiO<sub>2</sub> with poly(acrylic acid)-polystyrene block copolymer hyper-dispersants. It is proved that the end group of polymers will form some bond interactions with TiO<sub>2</sub> particles, which improves the stability between polymer and TiO<sub>2</sub> particles and then improves the dispersion of TiO<sub>2</sub> in water.



**Figure 6.**  
 The anchorage form of hyper-dispersant on particle surface: (a) single-point, (b) multipoint, and (c) co-anchoring with a surface synergist.



**Figure 7.**  
The scheme of particle dispersion by using hyper-dispersant.

Anchoring group	Electronegativity	Section width of anchoring group (nm)
-OH	3.9	0.22
-NH <sub>2</sub>	3.7	0.36
-SH	2.6	0.37
-SO <sub>3</sub> <sup>-</sup>	4.33	0.58
-PO <sub>4</sub> <sup>2-</sup>	4.86	0.60
-COOH	4.1	0.52
	4.88	0.74
	4.15	0.22
	3.8	0.65

**Table 5.**  
Electronegativity and section width of the anchoring group [42].

Zhang et al. [44] synthesized three hyper-dispersants: nonterminated, carboxyl-terminated, and polyethylene imine-grafted poly(hydroxyl carboxylic acid) ester. It is found that polyethylene imine-grafted hyper-dispersant has the best dispersion performance in nano-TiO<sub>2</sub>/resin solution dispersion systems.

A novel acrylic polyester hyper-dispersant containing methacrylic acid (MAA), butyl acrylate (BA), and 3-pentadecylphenyl acrylate (PDPA) was polymerized by Liu et al. [45]. This hyper-dispersant was used to disperse TiO<sub>2</sub> in a nonpolar solvent system. The results showed that the viscosity and particle size of suspensions were affected by monomer ratio and molecular weight. The optimum monomer ratio and molecular weight were MAA: BA: PDPA = 1:10:1.2 (wt%) and 6000, respectively. Liu et al. [46] further reported the effects of acrylic polyester hyper-dispersant on the

Polymer	Solvent chain structural unit	Flexibility	Solubility parameter $/J^{0.5}m^{-1.5}$
Polyethylene glycol	$OH \left[ CH_2 - CH_2 - O \right]_n H$	Good	1.88~2.49
Polyvinyl alcohol	$\left[ CH_2 - \underset{\substack{  \\ OH}}{CH} \right]_n$	Good	2.58~2.91
Polyacrylamide	$\left[ CH_2 - \underset{\substack{  \\ CONH_2}}{CH} \right]_n$	Good	2.65
Polyacrylic acid	$\left[ CH_2 - \underset{\substack{  \\ COOH}}{CH} \right]_n$	Good	2.44
Polymethylacrylic acid	$\left[ CH_2 - \underset{\substack{  \\ COOH}}{\overset{\substack{CH_3 \\  }}{C}} \right]_n$	General	1.86~2.64
Polymaleic Anhydride	$\left[ \underset{\substack{  \\ O=C}}{CH} - \underset{\substack{  \\ O=C}}{CH} \right]_n$	Bad	1.58~2.83
Polyvinylpyrrolidone	$\left[ CH_2 - \underset{\substack{  \\ N \\ / \quad \backslash \\ CH_2 \quad C=O \\ \backslash \quad / \\ CH_2 - CH_2}}{CH} \right]_n$	Very bad	2.30~2.62

**Table 6.**  
 Solubility parameters of some polymer structural units [42].

dispersion of TiO<sub>2</sub> in different organic solvents. The results showed that acrylic polyester hyper-dispersant adsorption onto TiO<sub>2</sub> is spontaneous and physical.

#### 4. Conclusion and prospects

As a critical pigment, TiO<sub>2</sub> has a considerable application market. However, due to the crystal defects, there is a photocatalytic active site on the surface of TiO<sub>2</sub>. After absorbing ultraviolet light, free radicals are produced, causing organic compound degradation in the surrounding TiO<sub>2</sub>. Besides, TiO<sub>2</sub> particles are easy to agglomerate

and are dispersed poorly in the organic matrix due to the high specific surface area. The surface inorganic/organic modification of  $\text{TiO}_2$  is an excellent choice to overcome the drawbacks of  $\text{TiO}_2$ . The coating films on the surface of  $\text{TiO}_2$  can effectively inhibit the oxidative degradation of the organic matrix and improve the dispersion of  $\text{TiO}_2$ , finally improving pigmentary properties of  $\text{TiO}_2$ , such as whiteness, hiding power, light resistance, and weather resistance. With the development of the economy, the demands for applying  $\text{TiO}_2$ , such as high weather resistance, light resistance, and dispersion stability, are gradually increased. Thus, the coating treatments of  $\text{TiO}_2$  are an essential strategic development direction in the future.

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