

Surface characteristics of hydrous silica-coated TiO₂ particles

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Abstract

The surface characteristics of hydrous silica-coated TiO₂ particles are experimentally studied. Different analytical techniques were used to characterize the Si oxide coatings on TiO₂ particles. The high-resolution transmission electron microscope (HRTEM), ζ-potential analyzer and X-ray photoelectron spectroscope (XPS) analyses show that hydrous silica is continuously coated on the surface of TiO₂ particles. From the chemical shift of binding energy of O 1s and Ti2p_{3/2} on coated particles and FTIR analyses of absorption band, it is inferred that Si oxide in the coating film is combined onto TiO₂ particle surface through chemical bond of Ti–O–Si. The electrokinetic behavior of TiO₂ particles can be modified significantly by dense film coating. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Titanium dioxide; Coating; Silica; Surface modification

1. Introduction

Fine TiO₂ particles have been widely used as a white pigment in the paint, plastic and paper industries, etc., for their excellent pigmentary properties. TiO₂ particles are easily pulverized and the molecules of organic polymer in paint film are easily cracked due to strong photocatalysis of TiO₂ particles, especially when they are exposed under ultraviolet, e.g. under sunlight. Thereafter, the paint becomes scoured off easily and undergoes yellow discoloration. These characteristics severely restrict the performance of the excellent optical properties of TiO₂ particles. Therefore, TiO₂ particles are usually coated with inert shell to prevent the TiO₂ photocatalysis taking effect. A well inorganic coating can increase the weather durability of TiO₂ particles by sealing the photocatalysis inside the particle with a dense film.

The coated TiO₂ particles exhibit similar surface characteristics of coating materials. Hydrous silica and hydrous alumina are the most commonly used coating materials of inorganic coating for TiO₂ particles [1,2]. Hydrous silica film coating can improve both the pigment weather durability and the dispersion properties. Two kinds of silica

film on well-coated particles can be obtained at different coating conditions [3,4]. One is a dense film, which has a uniform thickness and condensed structure. The photocatalysis of TiO₂ can be sealed in the shell completely, by which the weather durability of the paint can be remarkably increased. The other is a porous sponge film, which exhibits excellent optical characteristics due to the light multireflection in the porous film. Coating on TiO₂ particles with an average diameter of 0.3 μm to get a film of nanoscale is the key for preparation of high-rank TiO₂ pigment. In the coating process, the TiO₂ particles serve as a substrate for nucleation of precipitating materials, forming a thin amorphous film. The precipitation rate of coating materials affects the coating process and coating quality [5]. It was mentioned that silica is hydrated and bound upon the surface of the particles. The condensation of the silicic acid forms the coating film. However, there was no evidence to support this [6]. The mechanism of the coating process is still kept unclear. Many literature focus on the optimum conditions with different coating process for excellent quality of pigmentary TiO₂ particles [7–14]. There is no detail report about the combination at the interface and the coating film structure.

The present work studies the structure, properties and mechanism of silicon oxide coating of dense film on TiO₂ particles by using high-resolution transmission electron microscope (HRTEM), X-ray photoelectron spectroscope (XPS), Fourier transform infrared spectrum (FTIR) and ζ-potential analyzer.

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2. Experimental

2.1. Materials

All chemicals used in the experiments were of analytical reagents (AR) grade. A polysilicate solution with a $\text{SiO}_2/\text{Na}_2\text{O}$ ratio of 3.14 and sulfuric acid were employed. Commercial TiO_2 particles from the sulfate process without coating, in which the TiO_2 particles are produced from the hydrolysis of TiOSO_4 and subsequent calcination, were used in experiments [15]. The mean diameter of the TiO_2 particles is 300 nm. The particles are rutile crystal and nonporous, with a BET surface area of $6.54 \text{ m}^2/\text{g}$.

2.2. Sample preparation

The experiments are carried out in a cylindrical reactor, in which the temperature and pH are inspected on-line through a thermometer and a pH electrode, respectively. TiO_2 powders are dispersed in deionized water at a concentration of 200 g/l with dispersant of polysilicate. The slurry is stirred strongly and adjusted to $\text{pH} = 9.5$ by titrating polysilicate solution. The slurry temperature is kept at 85°C and stirring is kept on in the whole coating process. One molar of polysilicate solution and H_2SO_4 solution of 10 wt.% are titrated into the slurry. The $\text{SiO}_2/\text{TiO}_2$ weight ratio is set at 3%. The titration speed is kept constant. After the titration is finished, the slurry is aged under stirring condition for 2 h at $\text{pH} = 9.0$. Thereafter, it is filtered and washed with deionized water to remove SO_4^{2-} and then dried up at 120°C . The above pH value, temperature, concentration and aging time are optimized parameters for getting dense film coating of TiO_2 particles in experiments [16].

2.3. Sample characterization

The morphology and structure of hydrous silica-coated TiO_2 particles are checked by HRTEM (JEOL-2010F, Japan). The chemical compositions of the particle surface and the chemical bond action at the interface of coating film and the particle surface are determined by XPS (PHI-5300, PA, USA). The interfacial structure is also checked by FTIR (NICOLET 5DX, Germany). The ζ -potential–pH curve of TiO_2 particles is obtained through a Zeta-plus potential analyzer measurement (Brookhaven Instruments, USA).

3. Results and discussion

3.1. Structure of coated particles

Fig. 1 shows the HRTEM image of the hydrous silica-coated TiO_2 particle. Fig. 1a shows that a thin film is

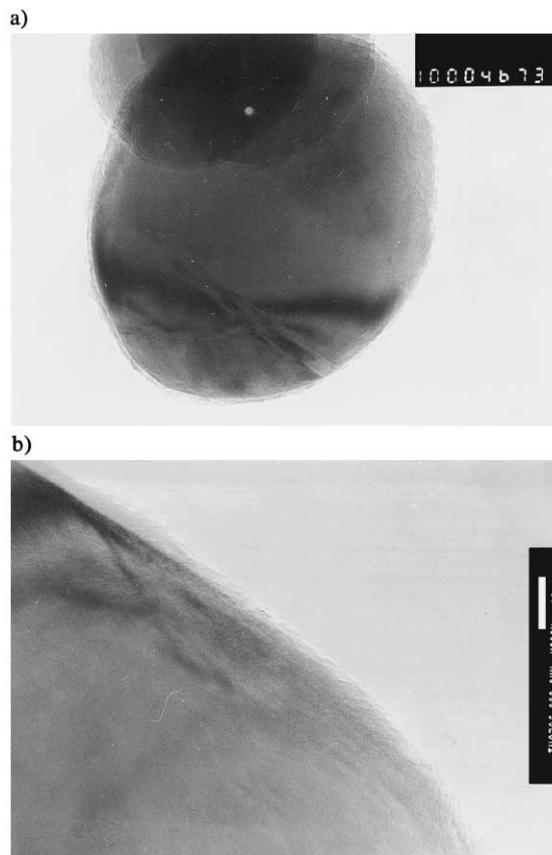


Fig. 1. HRTEM images of hydrous silica-coated TiO_2 particle with different amplifications.

continuously coated on the particle surface. The local image with higher amplification is shown in Fig. 1b. The hydrous silica film can be seen from the upper part, and the crystal lattice image of the titanium dioxide can be seen in the lower part. It shows that the hydrous silica film is formed on the surface of TiO_2 particles. The thickness of the hydrous silica film is estimated at about 4 nm.

3.2. Surface composition

The surface composition of TiO_2 particles can be qualitatively determined by energy dispersion spectrum (EDS), which is shown in Fig. 2. By comparing the EDS analysis on the surface and matrix, the presence of silicon is identified in the coated TiO_2 particles, and the concentration of silicon at the particle surface is higher than that in the matrix. The relative surface compositions on the coated and uncoated particle expressed quantitatively as atom percentage, derived from the XPS intensities, are shown in Table 1. Si component is enriched on the surface of coated particles. It is concluded that Si oxide is coated on the surface of TiO_2 particles. Since the coating material is hydrous silica, H_2O component exists in the coating film.

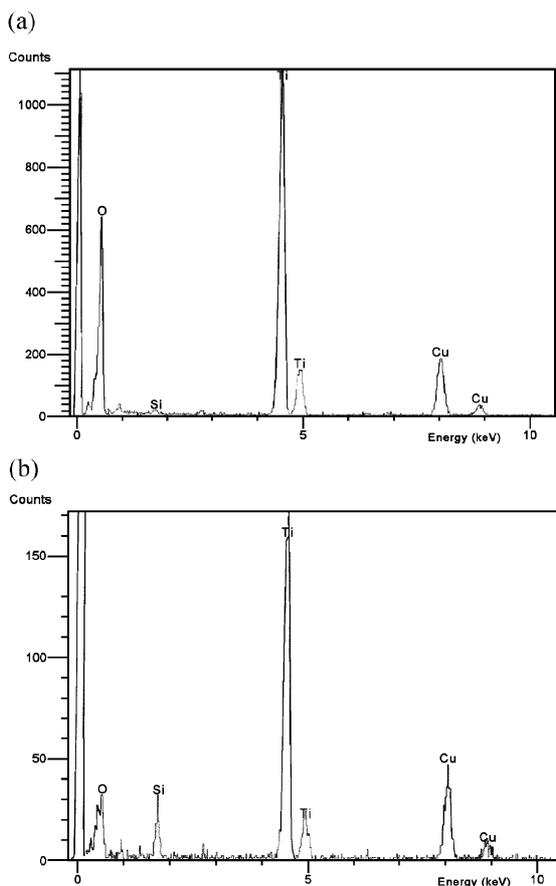


Fig. 2. EDS analysis of hydrous silica-coated TiO_2 powders: (a) matrix; (b) surface.

From thermogravimetric analysis (TGA) in N_2 atmosphere, the weight loss of sample is 0.32% from 120 to 600 °C, which shows that the structure water content of silicon film coated on TiO_2 particles is 0.32%. Considering the added amount of Si is 3% (weight of SiO_2 over TiO_2), the molecular composition of coating film can be roughly estimated as $\text{SiO}_{2.36}\text{H}_{0.72}$.

3.3. Analysis of interfacial structure

Fig. 3 shows the FTIR spectra of pure and hydrous silica-coated TiO_2 powders. It can be seen that compared with the spectrum of pure TiO_2 , an absorption band in 1000–1300 cm^{-1} occurs in the spectrum of coated TiO_2 powders. It is known that the O–Si asymmetric flexible vibration of ordinary silicic acid leads to the absorption

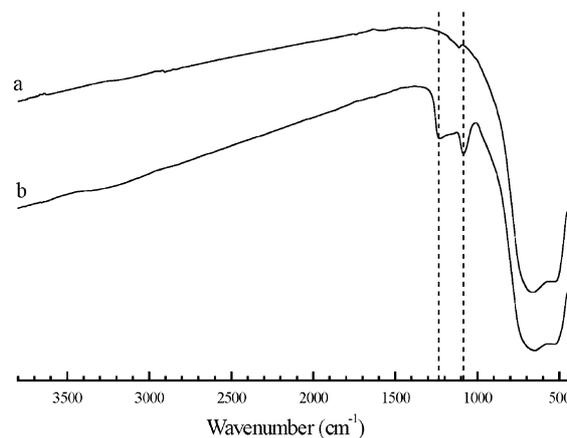


Fig. 3. FTIR analysis of samples: (a) TiO_2 ; (b) hydrous silica-coated TiO_2 .

band in 800–1000 cm^{-1} , and that of amorphous silica leads to the absorption band in 1000–1200 cm^{-1} . But in this sample, there is chemical action between the coated hydrous silica and the surface of TiO_2 particles. Under the effect of Ti atom, the symmetry of Si–O tetrahedron is broken. The original simple band splits or the noninfrared vibration is changed into infrared vibration, leading to the appearance of a new absorption band, and the vibration frequency shifts to high frequency. Therefore, this absorption band in 1000–1300 cm^{-1} is inferred by O–Si asymmetric flexible vibration.

O 1s spectra of pure and coated TiO_2 powders are shown in Fig. 4. The binding energies of O 1s peaks for pure TiO_2 are 529.3 and 532.3 eV. The 529.3-eV peak is much stronger than the 532.3-eV peak. For the hydrous silica-coated TiO_2 powders, the 533.2-eV peak is stronger than the 530.1-eV peak in O 1s binding energy. Comparing Fig. 4 with standard spectra, it is known that the O 1s peak of 533.2 eV is the binding energy for SiO_2 . The

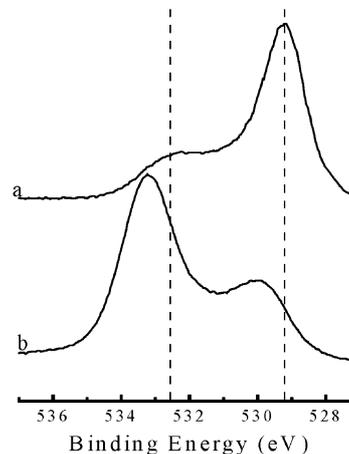


Fig. 4. O 1s XPS spectra of samples: (a) TiO_2 ; (b) hydrous silica-coated TiO_2 .

Table 1
The surface compositions of samples from XPS analysis (at.%)

Sample	Ti	Si	O
TiO_2	22.31	0	77.69
Hydrous silica-coated TiO_2	8.17	15.55	76.29

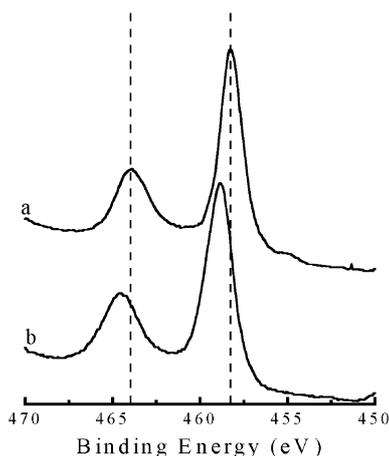


Fig. 5. Ti 2p XPS spectra of samples: (a) TiO_2 ; (b) hydrous silica-coated TiO_2 .

stronger peak of 533.2 eV is attributable to the SiO_2 coating on the particle surface. It is deduced that the 530.1-eV peak of O 1s in coated TiO_2 resulted from a chemical shift of 529.3-eV peak of O 1s in pure TiO_2 . In the coated TiO_2 powder, it is inferred that Si is combined onto the surface of TiO_2 , forming a Ti–O–Si bond. Because the electronegativity of Si is greater than that of Ti, O 1s peak for TiO_2 has a chemical shift of +0.8 eV.

Ti2p spectra of pure and coated TiO_2 powders are shown in Fig. 5. The binding energy of $\text{Ti}2p_{3/2}$ peak for pure TiO_2 is 458.2 eV. $\text{Ti}2p_{3/2}$ peak for silicon-coated TiO_2 is 458.9 eV, 0.7 eV greater than the $\text{Ti}2p_{3/2}$ peak of pure TiO_2 . It is also an evidence for deducing that Ti–O–Si bond forms. The decrease of the electron density around Ti atom results from the greater electronegativity of Si via O acting on Ti. The shielding effect is weakened, and then the binding energy is increased.

Binding energy values from XPS peaks are given in Table 2. From the chemical shift of $\text{Ti}2p_{3/2}$, O 1s peaks and FTIR spectra analysis, it can be concluded that Si oxide is combined onto the surface of TiO_2 particles through chemical bond. Ti–O–Si bond forms at the interface of hydrous silica coating film and TiO_2 particle surface.

3.4. Electrokinetic behavior

In order to check the surface coating effects, the ζ -potential–pH curves of pure TiO_2 , coated TiO_2 , TiO_2

Table 2
Binding energy of the measured photoemission peaks (eV)

Sample	Ti 2p _{3/2}	Si 2p	O 1s	
			I	II
TiO_2	458.2		529.3	532.3
Hydrous silica-coated TiO_2	458.9	103.9	530.1	533.2

mixed with SiO_2 colloid and pure SiO_2 particles are shown in Fig. 6. The sample of TiO_2 mixed with SiO_2 colloid is prepared by adding 3% SiO_2 colloid (of TiO_2 by weight) into TiO_2 slurry of the same solid concentration. The aqueous solution of the pure SiO_2 particles is the SiO_2 colloid without TiO_2 particles.

It can be seen that the coated TiO_2 has the similar electrokinetic behavior as pure SiO_2 particles. The isoelectric points (IEP) of both samples are roughly the same as 2.5. The ζ -potential value of coated TiO_2 particles at pH = 7 is about –56 mV, whereas that of pure TiO_2 particles is about –24 mV, which enables the dispersion of coated TiO_2 particles to be much easier than noncoated particles. It shows that the surface characteristics of TiO_2 particle are significantly modified after coated with hydrous silica. The surface structure of hydrous silica-coated TiO_2 particles is –Si–OH. When pH in the aqueous solution is lower than IEP, –Si–OH₂⁺ forms and the surface possesses positive charge. When pH is higher than IEP, –Si–O[–] forms and the surface possesses negative charge.

The ζ -potential–pH curve and IEP for TiO_2 mixed with SiO_2 colloid are similar to those of pure TiO_2 particles. It infers that the nucleation coating could not modify the TiO_2 particles effectively. The process of adding SiO_2 colloid into TiO_2 slurry is similar to the situation of nucleation coating when the forming rate of hydrous silica controls improperly in the coating process. Part of SiO_2 colloid is adsorbed onto the surface of TiO_2 particles by electrostatic attraction and part of it remains in the solution. The particle surface can not be modified properly. Therefore, the surface characteristics of hydrous silica-coated TiO_2 powders are essentially different from the TiO_2 powders mixed with SiO_2 colloid.

Fig. 6 also shows that the surface electrokinetic behavior depends on the quality of surface coating. Dense film coating can seal the TiO_2 particles completely and improve the particle dispersion effectively. Whereas incomplete coating such as nucleation coating shows less modification effect on TiO_2 particles.

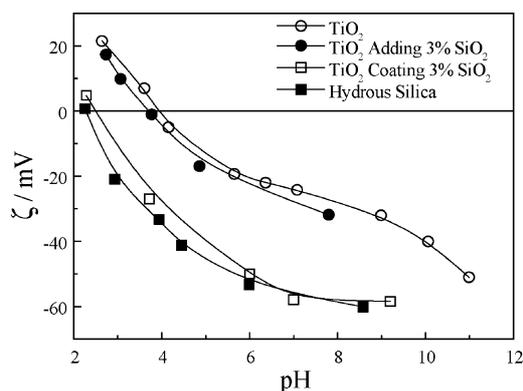


Fig. 6. The ζ -potential of pure and coated TiO_2 .

4. Conclusion

The experimental results show that a nanoscale film of hydrous silica is continuously coated on the surface of TiO_2 particles. The film composition is the condensation of hydrous silica.

Comparing the binding energies of $\text{Ti}2p_{3/2}$ and O 1s in pure and coated TiO_2 particles, it is concluded that the Si oxide is combined onto the surface of TiO_2 particles through chemical bond. Ti–O–Si bond forms at the interface of coating film and particle surface. The formation of Ti–O–Si bond breaks the symmetry of Si–O tetrahedron and results in the O–Si asymmetric flexible vibration, leading to the absorption band of coated particles shift to higher wave numbers.

The surface of TiO_2 particles is significantly modified after the film is coated with hydrous silica. Film-coated TiO_2 particles show the similar electrokinetic behavior as pure SiO_2 particles. The absolute value of ζ -potential of the film-coated TiO_2 particles in aqueous solution is remarkably increased, which enables the particle dispersion to be much easier, whereas incomplete coating such as nucleation coating shows less modification effect on TiO_2 particles.

References

- [1] R.L. Decolibus, U.S. 3,928,057, 1975.
- [2] H.W. Jacobson, U.S. 4,416,699, 1983.
- [3] A.L. Cui, T.J. Wang, Y. Jin, *Eng. Chem. Metall.* 20 (2) (1999) 178–181.
- [4] A.L. Cui, T.J. Wang, Y. Jin, *Chem. J. Chin. Univ.* 19 (11) (1998) 1727–1729.
- [5] U. Gesenhues, *J. Colloid Interface Sci.* 168 (1994) 428–436.
- [6] R.K. Iler, U.S. 2,885,366, 1959.
- [7] U. Gesenhues, *J. Colloid Interface Sci.* 168 (1994) 428–436.
- [8] M. Bruni, M. Visca, F. Garbassi, *Ind. Eng. Chem. Prod. Res. Dev.* 24 (1985) 579–586.
- [9] L.S. Johansson, T. Losoi, *Surf. Interface Anal.* 17 (1991) 230–236.
- [10] W.J. McGinnis, U.S. 3,410,708, 1968.
- [11] A.J. Werner, U.S. 3,437,502, 1969.
- [12] G.P. Fotou, T.T. Kostas, B. Anderson, *Aerosol Sci. Technol.* 33 (2000) 557–571.
- [13] M.K. Akhtar, S.E. Pratsinis, *J. Mater. Res.* 9 (5) (1994) 1241–1249.
- [14] C.H. Hung, J.L. Katz, *J. Mater. Res.* 7 (7) (1992) 1861–1869.
- [15] G. Lailach et al., in: E. Bartholomé (Ed.), 4th edn., *Ullmanns Encyklopädie der technischen Chemie*, vol. 18, Verlag Chemie, Weinheim, 1972, p. 569.
- [16] A.L. Cui, *Studies on Process, Mechanism and New Reactor of Coating on Surfaces of Titania*. Doctoral Dissertation, Tsinghua University, 1999.