

## Organic Pigment Particles Coated with Titania via Sol–Gel Process

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This paper presented a novel method for the organic pigment coated with titania to improve the weatherability and dispersion ability in waterborne system. The organic pigment was first orderly adsorbed by two kinds of electrolyte: poly(sodium 4-styrenesulfonate) (PSS) and poly(diallyldimethylammonium chloride) (PDADMAC), then coated by titania via sol–gel process from titanium *n*-butoxide (TBOT). The effects of the numbers of polyelectrolyte layer, water content, and TBOT content on the morphology, particle size, surface element composition, porosity and pore size, thermal stability, and UV shielding property of the organic pigment were systematically investigated. It was found that only two layers of electrolyte adsorption and one-step coating of titania could obviously enhance the UV shielding property even thermal stability of the organic pigment. The thickness of the titania layer could be easily tailored by TBOT content.

### Introduction

Organic pigments have been extensively used in coatings, inks, and plastics industries or even in color filters<sup>1</sup> for electronics and communication apparatus since they have many advantages such as good photosensitivity, hue, brilliance, color strength, transparency, and so on. However, the limited hiding power, poor dispersion ability, and especially the poor weather durability are obviously the obstacles for organic pigments in many applications. Lots of methods have been explored so far to solve the above problems. For example, Lelu et al.<sup>2</sup> encapsulated an organic phthalocyanine blue pigment into polystyrene latex particles using a miniemulsion polymerization to improve its dispersion ability in aqueous system, Fei et al.<sup>3</sup> grafted a naphthol red pigment onto the inorganic silica core in order to enhance the heat resistance, color strength, and dispersing stability of the pigment. Krysztafkiewicz and Jesionowski<sup>4</sup> prepared organic pigments on inorganic substrates with particular reference to the modification of adsorbents by silane coupling agents, and organic–inorganic hybrid pigment with high color stability was obtained. Organic pigments could also be straightly coated with silica film as a protective shell by water glass process to improve the UV shielding property, stability, heat resistance, etc.<sup>5–7</sup> Recently, we successfully coated the organic pigments with colloidal silica particles using multistep layer-by-layer (LBL) assembly technique; the nanosilica content or the thickness of nanosilica shell could be modulated by the numbers of both polyelectrolyte layer and nanosilica layer. The nanosilica particles coated onto the surfaces of organic particles could obviously scatter the UV light especially after the second and the third layer of silica assembly.<sup>8</sup>

Up to now, however, there has been no report involved in titania-modified organic pigments, yet based on our best knowledge, although titania has been successfully coated on the surfaces of colloidal particles,<sup>9–11</sup> bonelike hydroxyapatite,<sup>12</sup> Mn–Zn ferrite particles,<sup>13</sup> latex particles,<sup>14,15</sup> etc. In the present work, we would further encapsulate the organic pigment

particles with titania shell via a sol–gel process of titanium *n*-butoxide (TBOT) since titania is believed to have better UV shielding property than silica. To successfully coat titania on the pigment surfaces, two kinds of polyelectrolyte, poly(sodium 4-styrenesulfonate) (PSS) and poly(diallyldimethylammonium chloride) (PDADMAC), were first sequentially adsorbed onto the surfaces of the organic pigment, then titania was wrapped the polyelectrolyte precoated organic pigment via a sol–gel process of TBOT. The effects of various preparation parameters such as the numbers of polyelectrolyte layer, water content, TBOT content, etc., on the morphology, particle size, surface atomic composition, porosity and pore size, thermal stability, UV shielding property, etc. of the organic pigment were investigated. It was found that only two layers electrolyte adsorption and one-step titania coating could already obviously improve the UV resistance even thermal stability of the organic pigment, which was greatly terser than the organic pigment particles coated with colloidal nanosilica particles via LBL assembly published in our previous paper.<sup>8</sup> In that work, six-layers polyelectrolytes were first adsorbed on the surface of the organic pigment particles and then three layers of nanosilica were coated on the modified organic pigment particles via LBL assembly method.

### Experimental Section

**Materials.** Polyelectrolytes: PDADMAC (Mw < 200 000) and PSS (Mw = 70 000) were obtained from Aldrich. TBOT (98.0%, AR grade), ethanol (95%, AR grade), and ammonia solution (25–28% ammonia content, AR grade) were purchased from Shanghai Chemical Reagent Co., Ltd. Deionized water was prepared in our lab. Organic pigment: Yellow 109 whose chemical structure was shown in Chart 1, was supplied by Ciba Company. All these ingredients were used without further purification.

**Preparation of Titania-Coated Organic Pigment.** *Dispersion of Organic Pigment.* A certain amount of PSS and 100 g of water were added into a 500-mL plastic vessel and stirred at room temperature for 10 min to prepare PSS solution, followed

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## CHART 1 Chemical Structure of Yellow 109

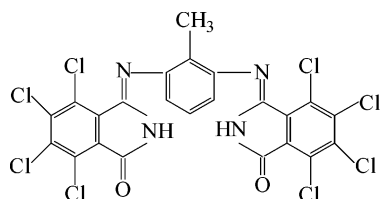


TABLE 1: Typical Experimental Information

sample no.	yellow 109 (g)	H <sub>2</sub> O (mol/L)	TBOT (mol/L)	temperature (°C)	ethanol (mL)
1	0.3	3.8	0.011	25	150
2 <sup>a</sup>	0.3	3.8	0.011	25	150
3	0.3	4.5	0.017	25	150
4	0.3	6.0	0.017	25	150
5	0.3	3.8	0.006	25	150
6	0.3	3.8	0.009	25	150
7	0.3	3.8	0.017	25	150
8	0.3	3.8	0.024	25	150
9	0.3	3.8	0.030	25	150

<sup>a</sup> Four layers of polyelectrolyte adsorbed organic pigment particles; the other two layers of polyelectrolyte adsorbed organic pigment particles

by adding of 10 g of Yellow 109, and then milled for 1 h in a bead miller with 1-mm ZrO<sub>2</sub> beads as milling media at a stirring speed of 3500 rpm to obtain stable organic pigment suspension with PSS as dispersant agent.

**Preparation of Cationic Organic Pigment Particles.** The superfluous PSS in the organic pigment suspension was removed through four cycles of centrifugation and deionized water washing. The obtained solid was redispersed into deionized water; the PSS adsorbed onto the surface of the organic pigment made the pigment particles negatively charged (proved by electrophoresis measurements). Then, PDADMAC was deposited onto the surfaces of the PSS precoated organic pigment particles by adding 1 g L<sup>-1</sup> aqueous polyelectrolyte solution (containing 0.3M NaCl). After 20 min adsorption, excess PDADMAC was removed by four cycles of centrifugation (12 000 rpm, 15 min) and deionized water washing. By repetition of the above steps, the polyelectrolyte multilayer could form on the surfaces of organic pigment particles according to experimental demand. This film could provide a uniformly charged surface and facilitate subsequent nanoparticle adsorption.<sup>16–18</sup> The outer layer was always PDADMAC, thus making the coated pigment particles positively charged.

**Preparation of Organic Pigment Encapsulated with Titania Shell.** The encapsulation of organic pigment via sol–gel process of TBOT was carried out in ethanol at room temperature using following typical process: a certain amount of cationic organic pigment paste was first diluted with ethanol then consecutively and equably dropped by the mixture of TBOT and ethanol over a period of 2 h, followed by magnetically stirred for another 10 h at room temperature to obtain titania-coated organic pigment suspension. The titania-coated organic pigment particles were then separated from the reaction medium by three cycles of centrifugation at ~8000 rpm, ethanol washing, and drying at room temperature for a couple of days in a vacuum oven. The detailed experimental information was summarized in Table 1.

**Characterization. Electrophoretic Mobility (EPM) Measurements.** Electrophoresis measurements were performed using a Brookhaven ZetaPlus  $\zeta$ -potential analyzer. All  $\zeta$ -potential measurements were performed on organic pigment redispersed in deionized water.

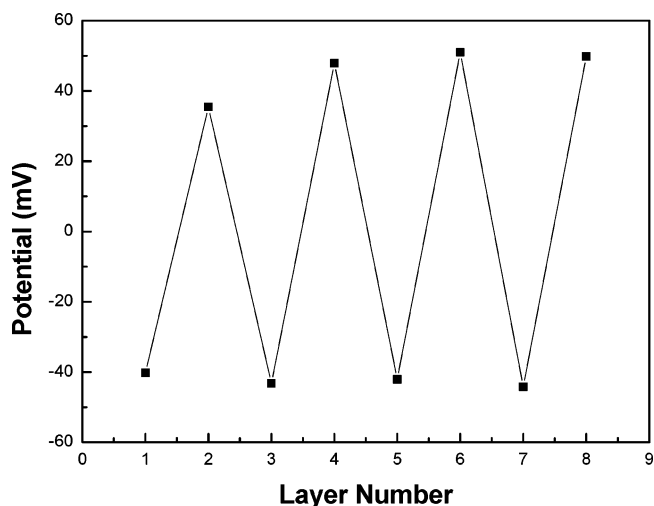


Figure 1.  $\zeta$ -potential as a function of polyelectrolyte layer numbers for PSS/PDADMAC-coated organic pigment particles. The odd layer numbers for PSS deposition and even layer numbers for PDADMAC deposition.

**Morphology of the Titania-Coated Organic Pigments.** The morphologies of titania coated organic pigments were observed by transmission electron microscopy (TEM, Hitachi H-600) and scanning electron microscopy (SEM, Philips XL30). The samples for TEM were sonicated in water for 5 min and then deposited onto carbon-coated copper grids and air dried before examination. For SEM observation, the titania coated organic pigments were first diluted and then dried on cover glass and finally sputter-coated with gold prior to examination.

**Particle Size Measurement.** Dynamic light-scattering experiments were carried out using N4 Plus particle size analyzer (Beckman Coulter Company, USA) to obtain the average particle sizes of the modified organic pigments.

**X-ray Photoelectron Spectroscopy (XPS) Survey.** A Perkin-Elmer PHI model 5000C was used for XPS analysis of the surfaces of the organic pigment. The exciting radiation was provided by an Al K $\alpha$  X-ray source operated at a constant power of 250W (14.0kV). Binding energy is 93.9 eV. The data were analyzed by PHI-MATLAB software.

**X-ray Powder Diffraction (XRD).** XRD diffractograms of the samples were taken on a Philips PW 1840 powder diffractometer using Ni-filtered Cu K $\alpha$  radiation ( $\lambda = 1.542 \text{ \AA}$ ).

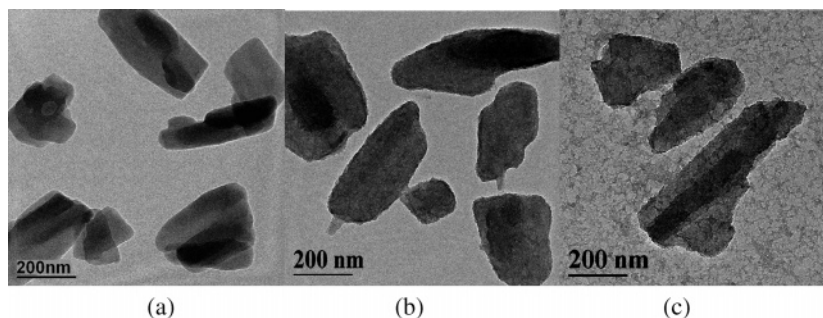
**Barrett–Emmett–Teller (BET) Analysis.** The nitrogen adsorption measurements were performed at 77K using an ASAP 2010 analyzer utilizing BET for calculation of specific surface areas and Broekhoff–de Boer model was used to calculate the pore size distribution.<sup>19</sup>

**Thermogravimetric Analysis (TGA).** The titania-coated organic pigment was heated on a Perkin-Elmer TGA-7 instrument in air from room temperature to 800 °C at a scan rate of 10 °C/min.

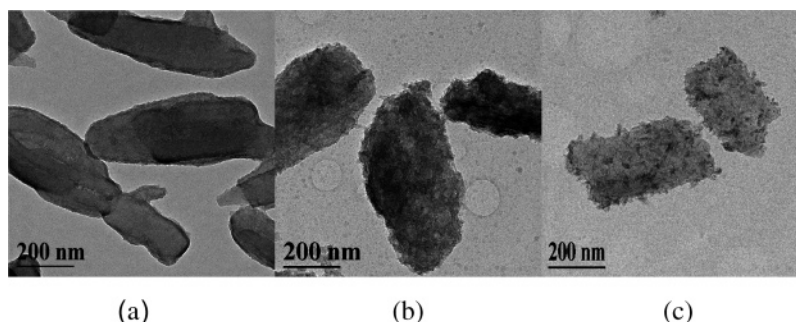
**UV–Vis Spectra.** The UV–vis spectra were obtained with a Lambda 35 spectrometer in the diffuse reflectance mode in a powder state.

## Results and Discussion

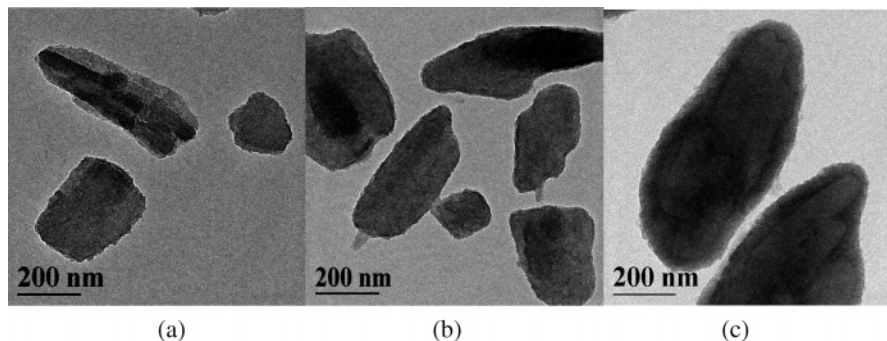
**Preparation Process of Organic Pigment Coated with Titania. The Effect of Polyelectrolyte Layers on the Morphology.** The  $\zeta$ -potential of the polyelectrolyte coated organic pigment particles as a function of polyelectrolyte layer numbers was measured in aqueous suspension at pH = 5.6 and demonstrated in Figure 1. The PSS-coated organic pigment particles



**Figure 2.** TEM images of original organic pigment (a); titania-coated organic pigment with two polyelectrolyte layers (sample 1) (b); four polyelectrolyte layers (sample 2) (c).



**Figure 3.** TEM images of the titania coating organic pigment with different content water: (a) 3.8 mol/L (sample 7); (b) 4.5 mol/L (sample 3); (c) 6.0 mol/L (sample 4).



**Figure 4.** TEM images of the titania-coated organic pigment with different content TBOT: (a) 0.006 mol/L (sample 5); (b) 0.009 mol/L (sample 6); (c) 0.024 mol/L (sample 8).

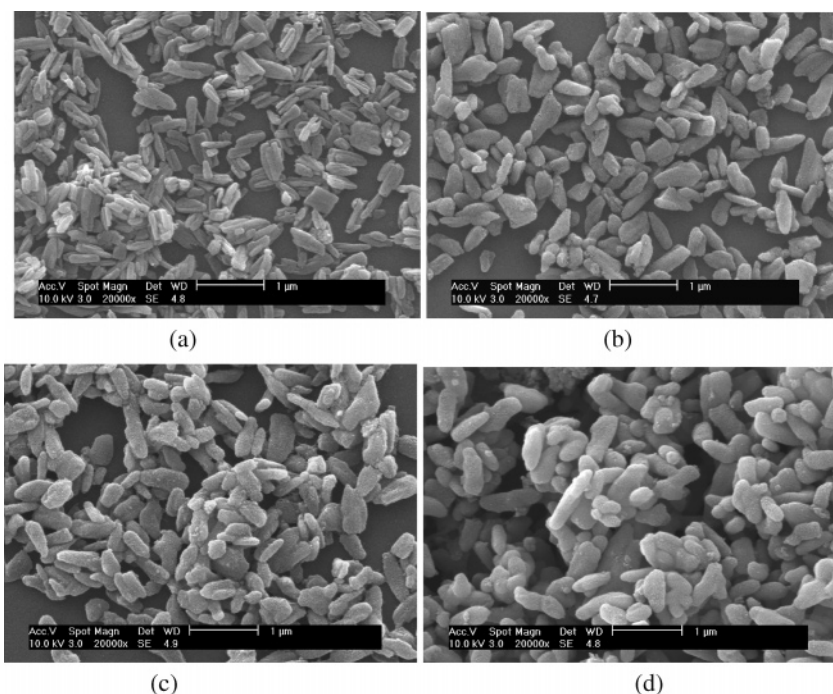
yielded a  $\zeta$ -potential of about  $-40.2$  mV, while the following PDADMAC deposition caused a reversal in  $\zeta$ -potential ( $35.46$  mV). Subsequent deposition of PSS on the PDDAMAC/PSS-coated organic pigment particles reversed the  $\zeta$ -potential again. Alternative  $\zeta$ -potential change was observed with the further deposition of each opposite charged polyelectrolyte, indicating that stepwise multilayer growth successfully occurred on the organic pigment particles. However, any quantitative conclusion could not be drawn from the  $\zeta$ -potential value because the value of the  $\zeta$ -potential was not proportional to the charge density, since the surface was composed of charges arranged in a layer of a finite thickness, and the  $\zeta$ -potential depended on the polyelectrolyte conformation at the surface.<sup>20–22</sup>

Figure 2 illustrated the TEM images of the original organic pigment particles and the titania-coated organic pigment particles precoated with two and four electrolyte layers (the samples 1 and 2 in Table 1). The original organic pigment particles which were virtually adsorbed by polyelectrolytes, showed very irregular size and homogeneous surface (Figure 2a). When the pigment particles were adsorbed by two polyelectrolyte layers then coated by titania, TEM picture revealed a uniform rough titania coating formed on the surfaces of the organic pigment particles, while very little titania particles were seen in the

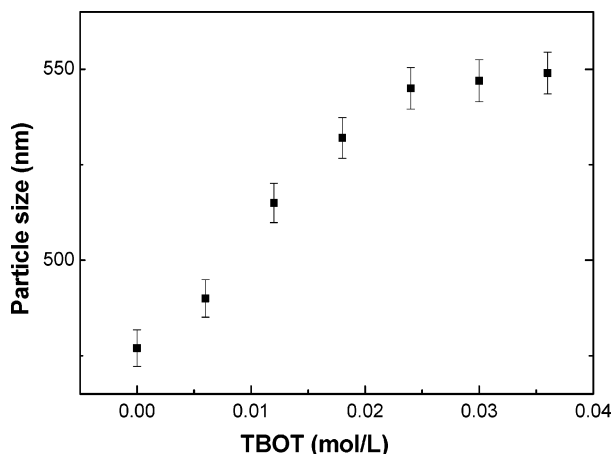
system (Figure 2b). However, when the organic pigment particles were adsorbed by four polyelectrolyte layers then coated by titania, the TEM picture observed not only a titania coating formed on the organic pigment particles surfaces but also some networklike titania particles in the system (Figure 2c). The organic pigment particles adsorbed by six or eight polyelectrolyte layers then coated by titania showed a similar morphology to the organic pigment particles adsorbed by the four polyelectrolyte layers then coated by titania (not presented here). This meant that two polyelectrolyte layers adsorption could guarantee the titania coating on the surfaces of the organic pigment particles efficiently, probably because more polyelectrolyte layers resulted in more hydration on the surfaces of pigment particles, decreasing the interaction between titania and the polyelectrolyte precoated organic pigment particles.<sup>23,24</sup>

**The Effect of Water Content on the Morphology.** Since water content strongly influences the hydrolysis and condensation of TBOT during the sol–gel process, it possibly have some impact on the morphology of the titania-coated organic pigment particles. Figure 3 demonstrated the TEM images of the titania-coated pigment particles at different water level. When water content was relatively low (3.8 mol/L), a dense titania coating formed on the surfaces of the organic pigment particles (see





**Figure 5.** SEM images of the titania-coated organic pigment with different content TBOT: (a) original organic pigment; (b) 0.006 mol/L (sample 5); (c) 0.009 mol/L (sample 6); (d) 0.024 mol/L (sample 8).



**Figure 6.** The effect of the loading content TBOT on the mean particle size of titania-coating organic pigment.

Figure 3a). However, as water content increased, more titania particles formed on the surfaces of the organic pigment particles (see parts b and c of Figure 3). This should be attributed to the faster hydrolysis and condensation of TBOT at higher water level.

**The Effect of TBOT Content.** Figure 4 displayed the TEM images of the titania-coated organic pigment with different TBOT content. Apparently, as more TBOT content was loaded, the particle size increased, accompanied by an increase in the thickness of the titania layer coating on the pigment particles. Figure 5 further presented the SEM images of the original organic pigment and the titania-coated organic pigments. Obviously, as more TBOT content was loaded, the increasing particle size of the titania-coated organic pigment was also observed. The mean particle size of the titania-coated organic pigment as a function of TBOT content was further determined by dynamic light-scattering particle size analyzer and manifested in Figure 6. The mean particle size of the original organic pigment was around 477 nm; as TBOT content increased, the mean particle size of the titania-coated pigment increased. When

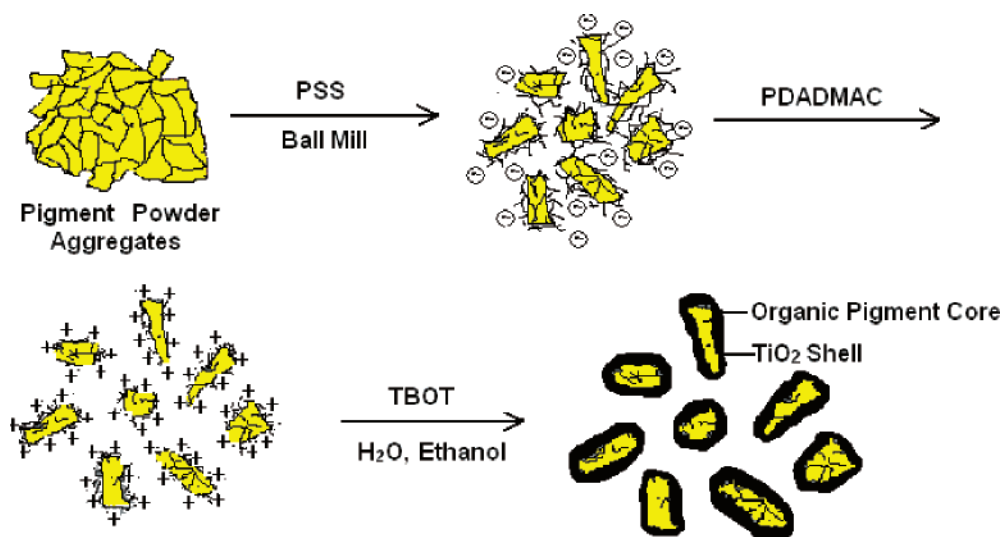
the TBOT content increased to 0.024 mol/L, the mean particle size of the titania coated pigment increased to 545 nm; however, when TBOT content further increased, the mean particle size of the titania coated pigment did not increase obviously, suggesting that the thickness of the titania coating on the surfaces of organic pigment particles could be tailored using TBOT content in a certain range; too much loading caused the formation of second-phase titania particles.<sup>25,26</sup>

On the basis of the above results and discussion, the proposed mechanism of titania coated on the surfaces of organic pigment could be described schematically as shown in Scheme 1.

**Surface Element Composition.** The X-ray surveys of  $\text{Ti}(2p_{1/2})$ ,  $\text{Ti}(2p_{3/2})$ , and  $\text{O}_{1s}$  of the titania-coated organic pigment with different thicknesses of titania coatings were shown in Figure 7. The binding energy of  $\text{Ti}(2p_{3/2})$  increased with the increasing thickness of the titania shell although all the binding energies of  $\text{Ti}(2p_{3/2})$  of titania-coated organic pigment were lower than the binding energy of the bare titania (458.8 eV),<sup>27</sup> see Figure 7a. The shift of the binding energy of  $\text{Ti}(2p_{3/2})$  should be attributed to the static interaction between titania and polyelectrolytes. The thicker the titania shell was, the closer the binding energy of  $\text{Ti}(2p_{3/2})$  of the titania-coated organic pigment was to that of bare titania, indicating that the interaction between titania and organic pigment became weaker. For  $\text{O}_{1s}$  spectra, as shown in Figure 7b, all the binding energies of  $\text{O}_{1s}$  for titania-coated organic pigments were between  $\sim 529.8$ – $531.0$  eV, higher than that of the  $\text{O}_{1s}$  peak of bare  $\text{TiO}_2$  (529.6 eV).<sup>27</sup> The broad  $\text{O}_{1s}$  regions of the titania-coated organic pigments were contributed by three peaks:  $\text{Ti}-\text{O}$  (529.6 eV) in  $\text{TiO}_2$ ,  $\text{O}-\text{H}$  (532.8 eV), and  $\text{C}-\text{O}$  bond (531.6 eV).<sup>28</sup> Similarly, with the increasing thickness of titania shell, the binding energy of  $\text{O}_{1s}$  increased, also suggesting a decreasing interaction between titania and pigment particles due to thicker titania coated on the surface of the organic pigment.

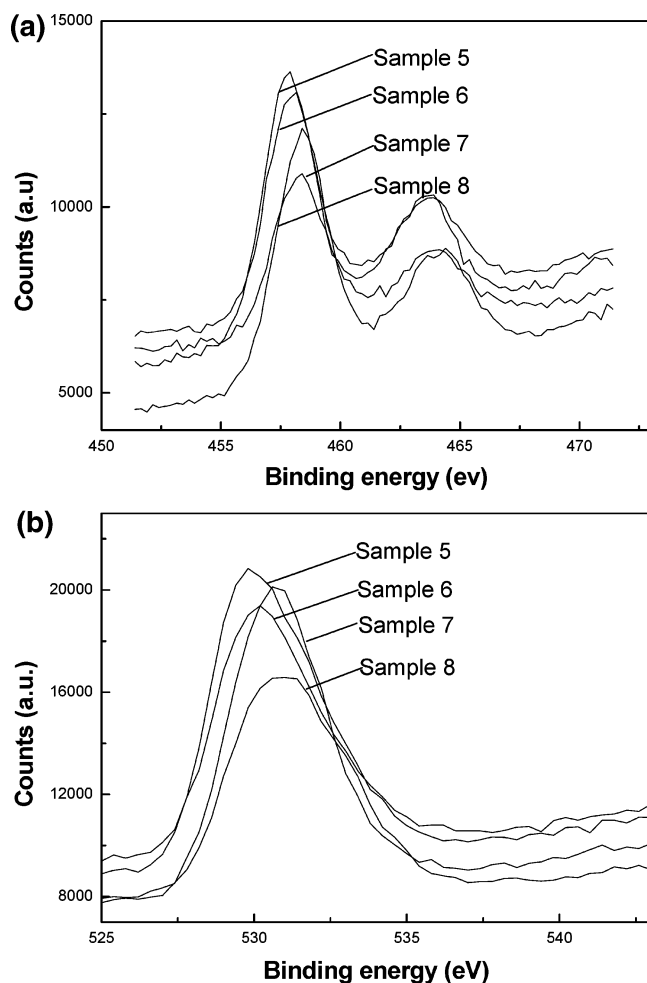
The surface atomic percentages of C, O, Ti, and Cl elements of the titania-coated organic pigment particles were calculated based on the X-ray survey at the takeoff angles of  $90^\circ$  and summarized in Table 2. Just as expected, the Ti atomic

## SCHEME 1: Mechanism for Preparation of Organic Pigment Particles Coated with Titania



percentage increased but the Cl atomic percentage decreased with increasing titania shell thickness, further confirming that more titania were coated onto the surfaces of organic pigment particles.

**XRD Analysis.** Figure 8 displayed the XRD spectra of the original organic pigment and the typical titania-coated organic pigment. Many diffraction peaks were observed in original organic pigment, which contributed to the characteristic peaks

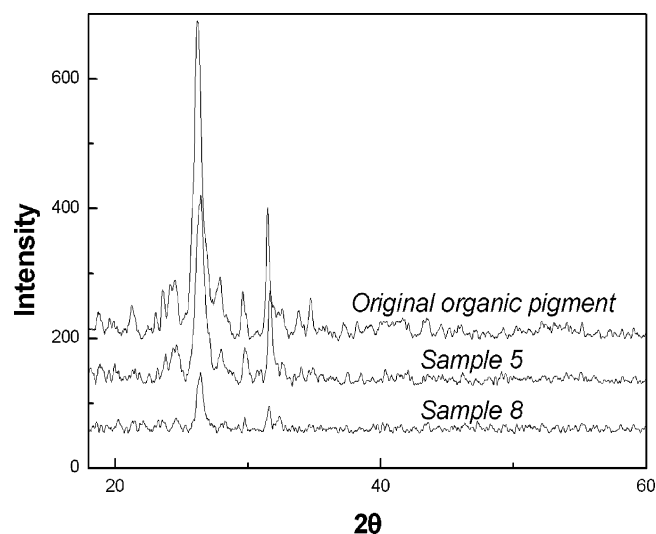


**Figure 7.** XPS surveys of  $\text{Ti}2p_{1/2}$ :  $\text{Ti}2p_{3/2}$  (a) and  $\text{O}1s$  (b) of the titania-coated organic pigments.

**TABLE 2: Surface Atomic Composition of the Titania-Coated Organic Pigment Particles**

sample no.	thickness of titania shell (nm) <sup>a</sup>	atomic content (%)			
		C	O	Ti	Cl
5	12	64.6	26.7	4.7	4.1
6	19	54.8	34.4	7.8	3.0
7	34	55.1	33.9	8.2	2.9
8	44	33.4	50.8	15.4	0.5

<sup>a</sup> The difference in the mean particle size of between titania coated pigment and the original pigment.



**Figure 8.** XRD patterns of original and the titania-coated organic pigments.

of the organic pigment, but these diffraction peaks weakened rapidly when titania coated on the surface of the organic pigment. Furthermore, no new characteristic peaks appeared at  $25.3^\circ$  and  $27.5^\circ$ , which corresponded to the anatase (101) and rutile (110) phases of the  $\text{TiO}_2$ , respectively,<sup>29,30</sup> indicating that the titania on the surfaces of the organic pigment particles still remained amorphous and was not transformed into anatase even rutile phase during coating organic pigment.

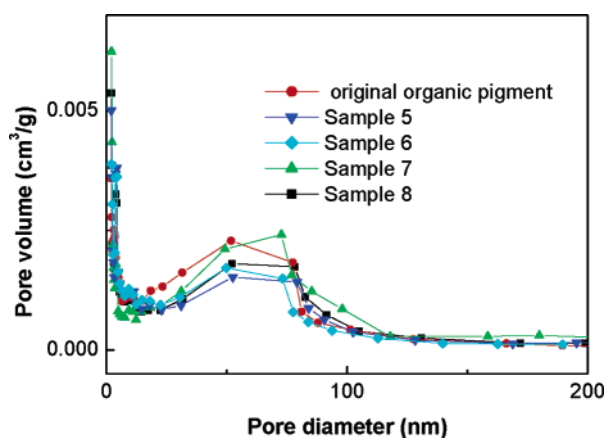
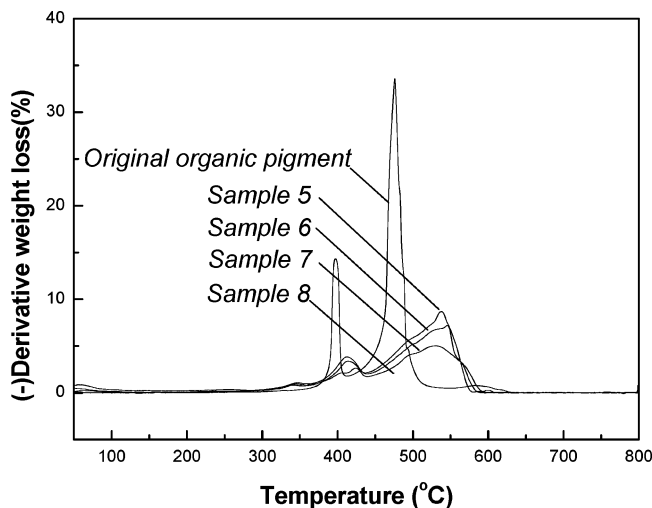
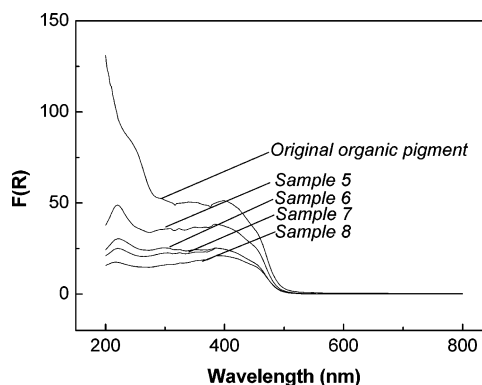
**Porosity and Pore Size.** The specific surface areas of the original organic pigment particles and the titania-coated organic pigment particles were determined by BET method and listed in Table 3. It was found that the specific surface areas of organic pigment particles decreased slightly when they were coated with

**TABLE 3: Specific Surface Areas of the Pigment Particles**

sample no.	BET area (m <sup>2</sup> /g)
original	29.3
5	27.3
6	26.3
7	27.3
8	25.7

titania. But no obvious change in specific surface area with thickness of titania coating was observed, suggesting that the titania layer coated on the surfaces of organic pigment particles was very dense, which could be further confirmed by the change in pore size, as shown in Figure 9. This was totally different from the coating of silica on organic pigment particles.<sup>8</sup>

**Thermal Property.** Figure 10 illustrated the differential TGA curves of the original organic pigment and the titania-coated organic pigment. Two weight loss stages were observed for original organic pigments: one was in the range of 350–425 °C resulting from the decomposition and carbonization of the pigment; another in the range of 425–525 °C attributed to the combustion of carbide. For the titania-coated organic pigment, one more weight loss stage occurred in the range of 310–350 °C due to the dehydroxylation and the removal of residual organics from the titania coating beside the same two weight loss stages as original organic pigment. Although the coating of titania did not postpone the onset decomposition temperature, the weight loss peaks of the titania-coated organic pigments

**Figure 9.** The pore size distribution of the titania-coated organic pigment.**Figure 10.** The differential TGA curves of the titania-coated organic pigments with different TBOT loading.**Figure 11.** Diffuse reflectance UV-vis spectra of the original and the titania-coated organic pigments.

became lower and wider, suggesting that the coating of titania could depress the decomposition rate of organic pigment, increasing the thermal stability of organic pigment. The more titania was coated, the much lower and wider the weight loss peaks were, indicating better thermal stability of organic pigment could be obtained.

**UV-Vis Spectra.** Figure 11 demonstrated the UV-vis diffuse reflectance spectra of the polyelectrolyte precoated and the titania-coated organic pigments. Since the spectra were determined in powder state in the diffuse reflectance mode, they should be able to denote the absorbing and scattering property of pigment. The lower the diffuse reflection absorption coefficient  $F(R)$  was, the higher the scattering property of the organic pigment was. For the polyelectrolyte precoated organic pigment, there was an obvious UV absorbance band especially below 270 nm. This absorbance band decreased remarkably when the organic pigment particles were coated with titania, indicating that the titania coating could obviously scatter the UV ray especially below 270 nm wavelength since low  $F(R)$  corresponded to high scattering property. The more TBOT content was loaded, the more titania was coated on the surface of the organic pigment, causing higher UV shielding property since titania has obvious UV absorbance.<sup>31,32</sup> Compared with the multilayer assembly technique of electrolytes and nanosilica coated on the organic pigment,<sup>8</sup> only two layers of electrolyte and one-step coating of titania could already reach the equal even better UV shielding property.

## Conclusions

This study demonstrated that the organic pigments could be successfully coated by titania through sol-gel process. Two kinds of polyelectrolyte (PDADMAC and PSS) were first sequentially adsorbed onto the surfaces of the organic pigment, then the dense titania layer was coated via the hydrolysis and condensation of TBOT. The adsorbed electrolyte layers and water content strongly influenced the morphology of the titania-coated organic pigment. The thickness of titania layer coated on the surface of the organic pigment could be controlled by the TBOT content. As the TBOT content increased, the mean particle size and surface Ti content of the coated pigment increased but the porosity and pore size did not change obviously. Only two layers of polyelectrolyte adsorption and one-step coating of titania could considerably improve the UV shielding property even thermal stability of organic pigment. Also, the coated titania should enhance the dispersion ability of organic pigment in water-borne system. This method was more laconic and efficient than the organic pigment particles coated with colloidal nanosilica via LBL assembly.

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