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Organic Pigment Particles Coated with Colloidal Nano-Silica Particles via Layer-by-Layer Assembly

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An organic pigment was successfully coated with colloidal silica particles using the layer-by-layer assembly technique to improve the weatherability and dispersion ability in waterborne systems. It was found that the nano-silica content or the thickness of the nano-silica shell could be modulated by the numbers of both polyelectrolyte layers and nano-silica layers. The first layer of nano-silica assembly obviously increased the particle size of the organic pigment, causing a relatively rough surface, an obvious augment in shell thickness, and a broad pore size distribution, but the second and the third layers of nano-silica assembly preferred to fill the pores caused by the first layer of silica, causing a relatively smooth surface, slight increases in shell thickness and surface Si content, and a narrow pore size distribution. The nano-silica particles coated on the surfaces of organic particles could obviously scatter the UV light especially after the second and third layers of silica assembly.

Introduction

Organic pigments have been extensively used in the paint, ink, and plastic industries since they have many advantages such as photosensitivity, color strength, excellent transparency, etc. However, the limited hiding power, poor dispersion ability, and especially the poor weather durability are obviously the obstacles for organic pigments in many applications. Many methods have been explored so far with the purpose of addressing the above problems. For example, Lelu et al.[1] encapsulated an organic phthalocyanine blue pigment into polystyrene latex particles using a miniemulsion polymerization to improve its dispersion ability in an aqueous system. But more modifications of organic pigments were involved in using silicon-based inorganic materials in recent years because of the inherent inert and super-high-durability properties of silicon-based materials. For example, Fei et al.[2] grafted a naphthol red pigment onto the inorganic silica core to enhance the heat resistance, color strength, and dispersion stability of the pigment. Krysztafkiewicz and Jesionowski[3] prepared organic pigments on inorganic substrates with particular reference to the modification of adsorbents by silane coupling agents, and an organic−inorganic hybrid pigment with high color stability was obtained. Organic pigments coated with silica as a protective shell are expected to improve the UV shielding property, stability, heat resistance, etc., which were studied by the water glass process.[4−6] However, this process obviously has some demerits: only a very thin SiO_2 layer from sodium silicate can form on the pigment surface; the reproducibility is also very poor.[4,7,9−11] Furthermore, the thin SiO_2 layer on the surface of the organic pigment may be not enough for enhancing the UV shielding property of the organic pigments. Here we present a modification method of organic pigments coated with nano-SiO_2 particles as a shell via the layer-by-layer assembly technique since nano-SiO_2 particles have UV scattering and/or absorbing characteristics. To our knowledge, there is no research on using nano-silica particles as a protective shell to coat organic pigments and also there are no reports on using the layer-by-layer assembly technique to coat organic pigments yet.

The layer-by-layer assembly technique has already been applied to fabricate core−shell materials, in which the aqueous colloidal particles are electrostatically adsorbed on the surfaces of charged polymeric and/or inorganic materials. Compared with the previous modification methods mentioned above, the method of the layer-by-layer technique to fabricate spherical particles has the advantage of easily diversifying the chemical composition, tailoring the thickness of the shell, and controlling the degree of the core surface coverage.[12,13] Several investigations with polystyrene beads,[14] formaldehyde particles,[15] inorganic particles,[16] and a biological cell[17]

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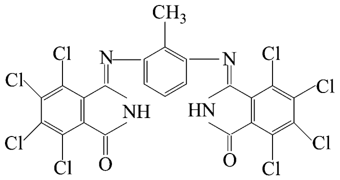
Chart 1. Chemical Structure of Yellow 109



as template cores for fabricating core–shell materials, hollow capsules, or hollow spheres were reported using the layer-by-layer assembly technique. However, no report has involved irregular, uncharged organic pigment particles coated with an inorganic shell by the layer-by-layer assembly technique yet.

To successfully coat nano-SiO_2 particles on the pigment surfaces, we first used two kinds of polyelectrolytes, poly(diallyldimethylammonium chloride) (PDADMAC) and poly(sodium 4-styrenesulfonate) (PSS), to be sequentially adsorbed onto the surfaces of the organic pigment and then coated by colloidal nano-SiO_2. The effects of various preparation factors such as the numbers of polyelectrolyte and nano-SiO_2 layers, the contents of nano-SiO_2 and organic pigment, the pH value, the adsorption time, etc. on the silica content adsorbed, the morphology and size of the composite particles, the shell thickness, etc. were investigated. It is found that it is very easy to tailor the thickness of the silica shell through controlling the numbers of polyelectrolyte layers and adsorbing cycles of SiO_2/PDADMAC. The UV-resistant performance of the organic pigment coated with the silica particles can be obviously improved.

Experimental Section

Materials. Polyelectrolytes PDADMAC (MW < 200 000) and PSS (MW = 70 000) were obtained from Aldrich. Sodium chloride (AR grade) was purchased from Shanghai Chemical Reagent Co., Ltd. of China. Deionized water was prepared in our laboratory. Silica aqueous sol (20 nm, pH 9.5, solid content 26.4 wt %) was obtained from Zhejiang Yuda Chemical Industry Co., Ltd. of China. The organic pigment Yellow 109, whose chemical structure is shown in Chart 1, was supplied by Ciba Co.

Preparation of Nano-Silica-Coated Organic Pigment. *Dispersion of the Organic Pigment*. A certain amount of PSS and 100 g of water were charged into a 500 mL plastic vessel and stirred at room temperature for about 10 min to prepare PSS solution, followed by charging with 10 g of organic pigment and then milling for about 1 h on a bead miller with 1 mm ZrO_2 beads as the milling medium at a stirring speed of 3500 rpm to obtain stable organic pigment paste with PSS as a dispersing agent.

Preparation of Organic Pigment Particles Coated with Nano-Silica. The silica-coated organic pigment particles were prepared by depositing multilayer polyelectrolyte films, followed by the alternate deposition of nano-SiO_2 particles and PDADMAC. The detailed preparation procedure is described as follows: First, the superfluous PSS in the organic pigment paste was removed through four cycles of centrifugation and deionized water washing. The obtained solid was redispersed into deionized water; thus, the surfaces of the organic pigment particles became negatively charged due to the PSS adsorbed (proved by electrophoresis measurements). Second, PDADMAC and PSS were subsequently and alternatively deposited onto the surfaces of the PSS-coated organic pigment by adding 1 g L^{-1} aqueous polyelectrolyte solution (containing 0.3 M NaCl). After 20 min of adsorption, excess polyelectrolytes were removed by four cycles of centrifugation (12000 rpm, 15 min) and deionized water washing and then redispersed into deionized water. Repeating the above steps, a polyelectrolyte multilayer film 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.[18–20] The outermost surface layer was always PDADMAC, thus making the coated particles positively charged. Third, nano-SiO_2 particles were adsorbed on the surfaces of the organic pigment by adding the SiO_2 aqueous sol to the suspension of the precoated organic pigment particles. The nano-SiO_2 particles were allowed to adsorb for 20 min under continuous stirring, and then the excess nano-SiO_2 was removed by four cycles of repeated centrifugation (6000 rpm, 15 min) and deionized water dispersion. The electrostatic interaction between the negatively charged silica nanoparticles and positive PDADMAC was utilized to build up the nanocomposite multilayers. Repeating the PDADMAC/SiO_2 layer-by-layer assembly steps, a multilayer SiO_2 shell could be obtained. The silica-coated organic pigments were designated as PE_i-jSiO_2, in which i indicates the number of polyelectrolyte layers and j the number of of nano-SiO_2 layers.

Characterization. *Amount of Silica Adsorbed on the Surface of the Organic Pigment*. The amount of nano-SiO_2 adsorbed on the surfaces of the organic pigment was determined on a Perkin-Elmer TGA-7 instrument in air and heated from room temperature to 800 °C at a scan rate of 10 °C/min.

Electrophoretic Mobility (EPM) Measurements. Electrophoresis measurements were performed using a Malvern Zetasizer 4. All ζ-potential measurements were performed on organic pigment redispersed in deionized water (pH $\approx$ 5.6).

Morphology of the Silica-Coated Organic Pigments. The morphologies of silica-coated organic pigments were characterized 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, deposited onto carbon-coated copper grids, and allowed to air-dry before examination. For SEM observation, the silica-coated organic pigments were first diluted and dried on a cover glass and sputter-coated with gold prior to examination.

Particle Size Measurement. Dynamic light scattering experiments were carried out using an N4 Plus particle size analyzer to obtain the average particle sizes of the modified organic pigments.

XPS Survey. A Perkin-Elmer PHI model 5000C was used for XPS analysis. The exciting radiation was provided by an Al Kα X-ray source operated at a constant power of 250 W (14.0 kV). The binding energy was 93.9 eV. The data were analyzed by PHI-MATLAB software.

BET Analysis. The nitrogen adsorption measurements were performed at 77 K using an ASAP 2010 analyzer utilizing the Barrett–Emmett–Teller (BET) model for calculation of surface areas, and the Broekhoff–de Boer (BdB) model was used to calculate the pore size distributions.[21]

Ultraviolet–Visible (UV–Vis) Spectra. The UV–vis spectra were obtained with a Lambda 35 spectrometer in the diffuse

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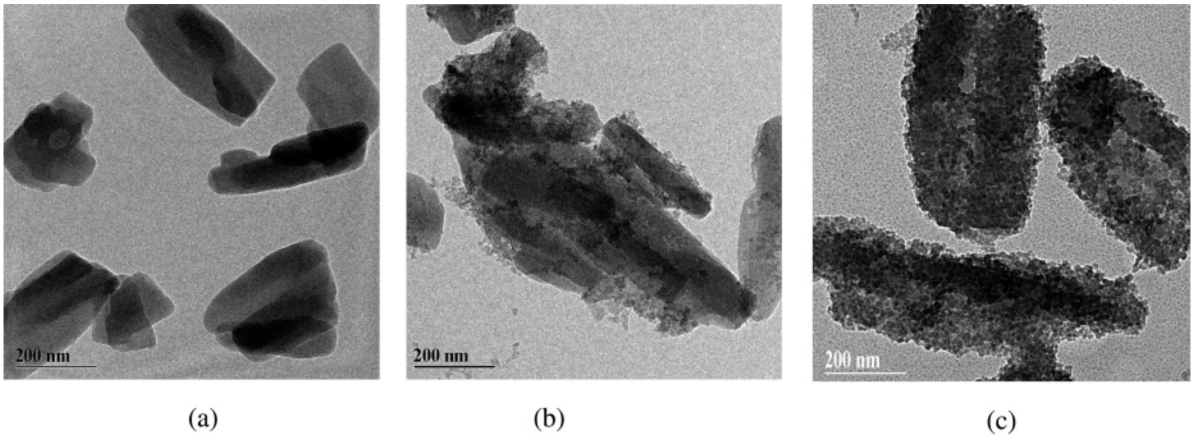


(a) (b) (c)

Figure 1. TEM images of uncoated organic pigment (a), PE_2-SiO_2-coated organic pigment (b), and PE_6-SiO_2-coated organic pigment (c).

reflectance mode and a Hitachi UV-3000 spectrometer in the transmission mode. The scattering spectra were determined in a powder state; the transmittance spectra were determined in an aqueous dispersion.

Results and Discussion

Preparation Process of Organic Pigments Coated with Nano-Silica Particles. Since the surfaces of the organic pigment were usually inert, the colloidal nano-SiO_2 particles obviously could not be directly adsorbed onto the surfaces of the organic pigment particles. Therefore, we first used polyelectrolytes PSS and PDADMAC to be sequentially and alternatively adsorbed onto the surfaces of the organic pigment and then coated by nano-SiO_2 particles. Figure 1a,b illustrates the TEM images of the original organic pigment and nano-SiO_2-coated organic pigment (PE_2-SiO_2). Obviously, nano-SiO_2 particles had been successfully adsorbed on the surfaces of organic pigment particles. However, the coverage by nano-SiO_2 particles was not sufficient for two layers of polyelectrolyte-pretreated organic pigment particles (PE_2). To enhance the coverage, pretreatment of organic pigments with more than two layers of polyelectrolytes was adopted. Figure 1c shows the TEM image of PE_6-SiO_2. Clearly, more nano-SiO_2 particles were adsorbed onto the surfaces of the organic pigment compared with PE_2-SiO_2. The effect of the number of polyelectrolyte layers on the amount of nano-SiO_2 adsorbed was determined by TGA and is demonstrated in Figure 2. It can be seen that the silica content adsorbed on the surfaces of the organic pigment increased with increasing number of polyelectrolyte layers. However, compared with six layers of polyelectrolytes, eight layers of polyelectrolytes just slightly enhanced the silica content, indicating the charge on the surfaces of the organic pigment was close to saturation. Considering that more layers of polyelectrolytes meant a more complicated process, organic pigment precoated with six layers of polyelectrolyte was employed for the preparation of the nano-SiO_2-coated organic pigment.

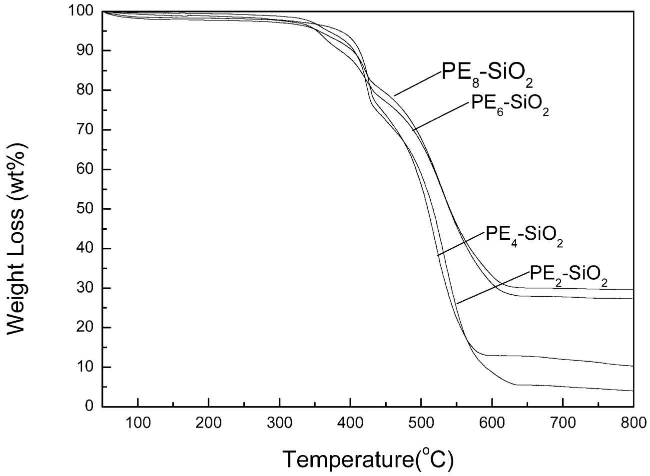


Figure 2. TGA curves of the one layer of silica coated organic pigment pretreated with different layers of polyelectrolytes.

Table 1. Effects of Various Condition Parameters on the Adsorbed Amount of SiO_2

$M_{pigment}$:M_{SiO_2}	pH value	time (min)	$C_{pigment}$ (wt %)	silica content[a] (wt %)
1:1	6	60	2.0	18.2
1:1	7	60	2.0	19.5
1:1	8	60	2.0	17.7
1:1	9	60	2.0	18.1
1:1	10	60	2.0	18.2
2:1	6	60	2.0	18.6
1:2	6	60	2.0	18.3
1:3	6	60	2.0	18.5
1:1	6	20	0.25	18.8
1:1	6	20	0.5	19.2
1:1	6	20	1.0	18.8

[a] Determined by TGA.

Besides polyelectrolyte layers, the influence of other reaction parameters, such as the concentrations of silica and the organic pigment, pH value, and adsorption, time on the adsorbed silica amount was also investigated and is summarized in Table 1. The data show that the silica content adsorbed onto the surfaces of the organic pigment changed little with the concentration of the silica sol or organic pigment and pH value. The adsorption of nano-SiO_2 particles was very quick to achieve a balance within 5 min, as illustrated in Figure 3. This means that the coverage of the organic pigment with silica was only related to the charge property of the organic pigment and nano-SiO_2 particles.

To further enhance the adsorbed silica content, multilayer adsorption of SiO_2 was carried out by sequential assembly of nano-SiO_2 and PDADMAC on polyelectrolyte-precoated organic pigments. Figure 4 displays the adsorption content of SiO_2 as a function of the number of SiO_2 assembly layers.

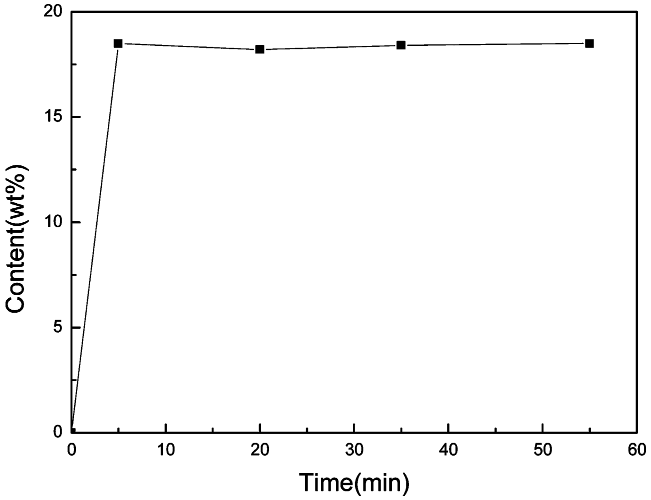


Figure 3. Effect of adsorption time on the adsorbed SiO_2 content.

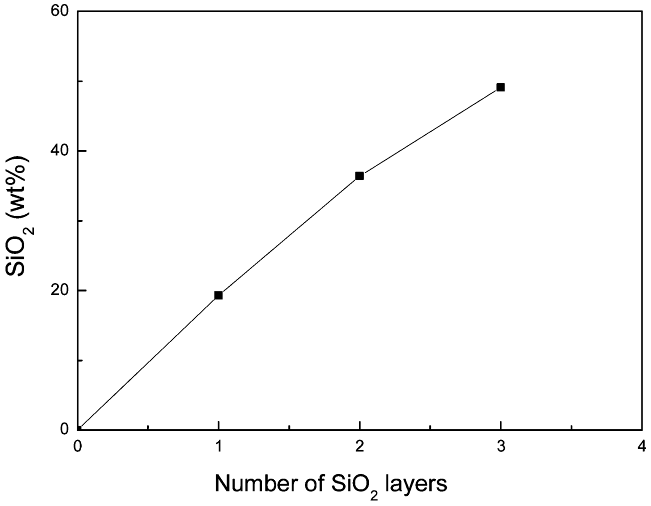


Figure 4. Variation of the adsorption SiO_2 content with the number of SiO_2 assembly layers.

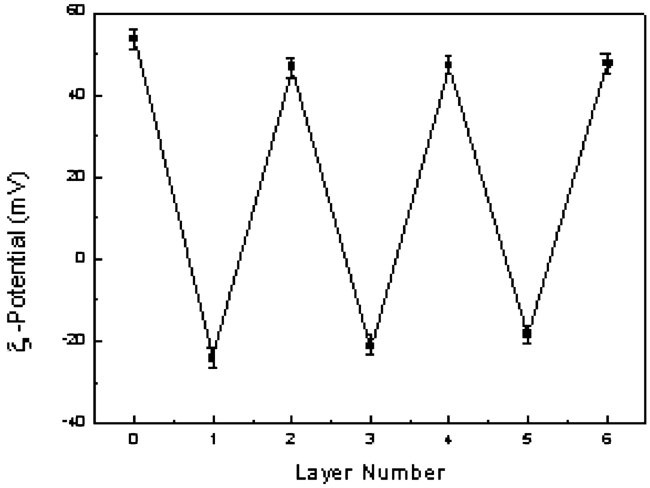


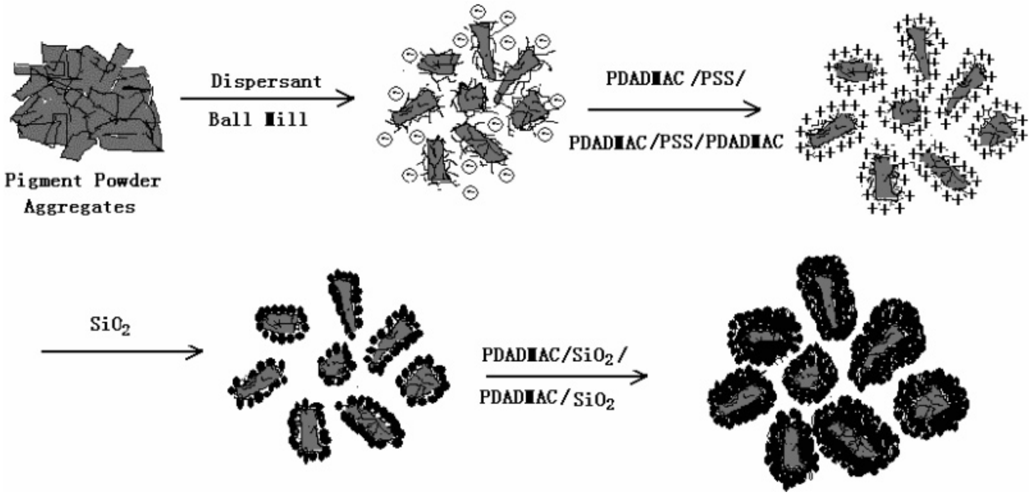
Figure 5. Change of the ζ-potential during the multilayer assembly process. A layer number of zero corresponds to the PE_6-coated organic pigment. The odd layer numbers correspond to SiO_2 adsorption and the even layer numbers to PDADMAC deposition. The multilayer-coated organic pigment particles were redispersed in deionized water (pH 5.6) prior to measurement of the ζ-potential.

It can be seen that the adsorption content of SiO_2 linearly increased with increasing number of SiO_2 assembly layers, confirming that multilayer adsorption of SiO_2 was an effective route to increase the adsorption content of SiO_2. Figure 5 further shows the change of the ζ-potential of the organic pigments during the multilayer assembly process. The assembly of SiO_2 and PDADMAC caused a reversal in sign of the ζ-potential with each deposition, suggesting that stepwise multilayer growth indeed occurred on the particles. In addition, the ζ-potential of silica-coated organic pigment particles was in the range of 45−55 mV (the six layers of polyelectrolyte-precoated organic pigment particles was around 53.6 mV) when PDADMAC was located at the outermost layer, whereas the ζ-potential was in the range of −15 to ∼−25 mV for the outermost SiO_2 layer, indicating that the organic pigment with PDADMAC as the outermost layer had much higher stability than that with nano-SiO_2 as the outermost layer. Therefore, the outermost layers of all the silica-coated organic pigments were finally coated with PDADMAC.

On the basis of the above results and discussion, the mechanism of coating of colloidal nano-SiO_2 particles onto the surfaces of the organic pigment can be schematically described as shown in Scheme 1.

Morphology and Particle Size. The morphologies of the original organic pigments and silica-coated organic pigments were examined using electron microscopes. Figure 6 shows

Scheme 1. Mechanism for Preparation of Organic Pigment Particles Coated with Colloidal Silica Particles



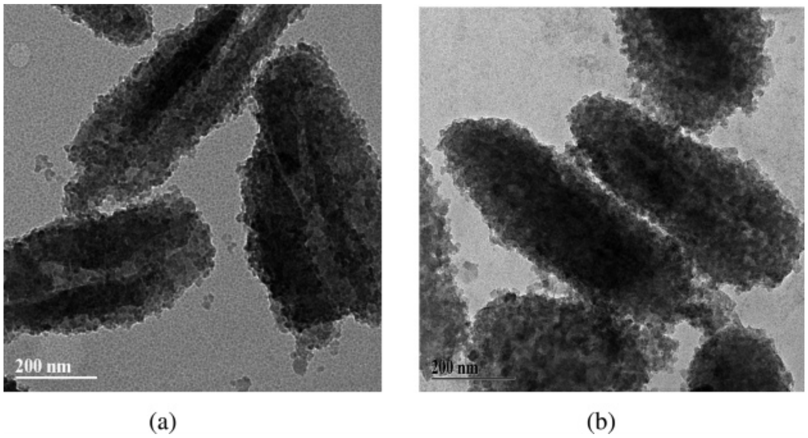


Figure 6. TEM images of PE_6-2SiO_2 (a) and PE_6-3SiO_2 (b).

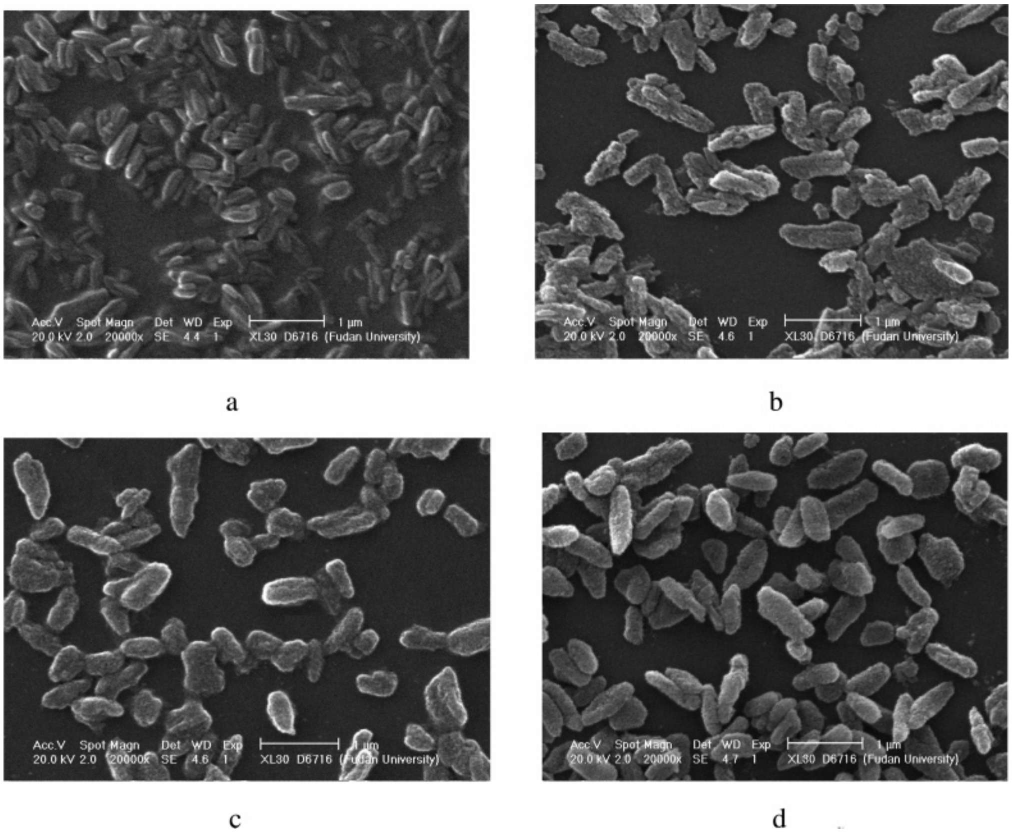
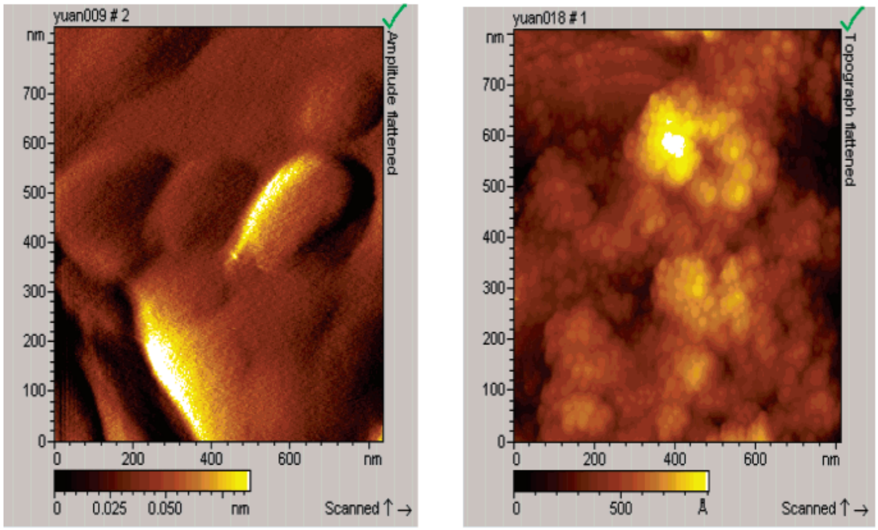


Figure 7. SEM images of uncoated organic pigment (a), PE_6-SiO_2-coated organic pigment (b), PE_6-2SiO_2-coated organic pigment (c), and PE_6-3SiO_2-coated organic pigment (d).

the TEM images of organic pigments coated with two and three layers of silica. It can be obviously seen that nano-SiO_2 particles were closely packed together but not to form a homogeneous film on the surfaces of the organic pigment at a high adsorbed silica level (see PE_6-SiO_2 in Figure 1c and PE_6-2SiO_2 and PE_6-3SiO_2 in Figure 6), while the silica particles were randomly distributed and incompletely covered the surfaces of the organic pigment at a relatively low adsorbed silica level (see PE_2-SiO_2 in Figure 1b). However, there was no obvious difference in morphology between the organic pigments deposited with different layers of SiO_2 (see PE_6-SiO_2, PE_6-2SiO_2, and PE_6-3SiO_2).

Figure 7 further presents the SEM images of the original organic pigments and silica-coated organic pigments. Compared with those of the uncoated organic pigment, the surfaces of the organic pigment coated with one layer of SiO_2 were relatively rough (see Figure 7b), but further SiO_2 multilayer deposition could improve the surface evenness of silica-coated organic pigment particles (see Figure 7c,d). Meanwhile, the first layer of SiO_2 deposition obviously increased the mean particle size of the organic pigment, but the second- and the third-layer SiO_2 coats only caused a slight increase in particle size. The changes in both the evenness and the mean particle size suggest that the second and the third SiO_2 layers prefer to fill the pore sites caused by the first layer of SiO_2 rather than locate on the first layer of SiO_2.

Figure 8 demonstrates the typical AFM images of the uncoated organic pigment and silica-coated organic pigment. The original organic pigment had a relatively smooth surface,



(a) (b)

Figure 8. AFM images of uncoated organic pigment (a) and PE_6-3SiO_2-coated organic pigment (b).

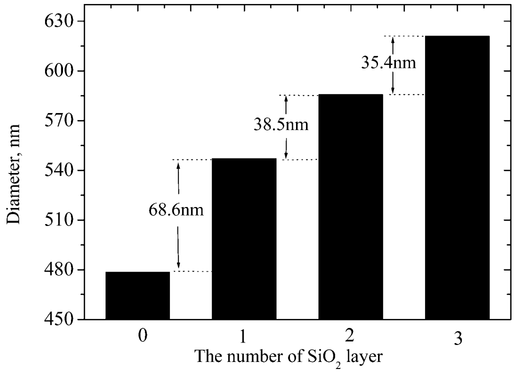


Figure 9. Effect of the number of SiO_2 layers on the mean particle size of the silica-coated organic pigment.

while the silica-coated organic pigment had a relatively rough surface covered with silica particles, which was consistent with the TEM results.

The particle sizes of the uncoated organic pigment and silica-coated organic pigment with different numbers of SiO_2 layers are displayed in Figure 9. Compared with that of the uncoated organic pigment, the particle size of the silica-coated organic pigment increased with increasing number of SiO_2 layers, suggesting that the thickness of the nano-silica layer surrounding organic pigment particles could be tailored using the layer-by-layer assembly process. Nevertheless, the increments of thickness for the second and third SiO_2 assembly layers were 38.5 and 35.4 nm, respectively, lower than the theoretical value of 44 nm (nano-SiO_2, 20 nm; the thickness of one layer of polyelectrolyte, 2 nm[17]); this should be attributed to some particles of the second and third SiO_2 layers preferring to fill the pore sites inside the first layer, just as observed by SEM.

Surface Atomic Composition. Figure 10 demonstrates the X-ray surveys of Si2p and O1s of the silica-coated organic pigment with different numbers of nano-SiO_2 layers. The binding energy of Si2p increased with increasing number of nano-SiO_2 layers (see Figure 10a) although all the binding energies of Si2p of the silica-coated organic pigment were lower than the binding energy of the bare silica (103.8 eV).[22] The shift of the binding energy of Si2p should be attributed to the static interaction between nano-SiO_2 particles and polyelectrolytes. The higher the number of SiO_2 layers adsorbed, the closer the binding energy of Si2p in silica-coated organic pigment was to that of bare silica, indicating that the interaction between nano-SiO_2 particles and organic pigment became weaker. For O1s spectra, as shown in Figure 10b, all the binding energies of O1s for silica-coated organic pigments were also smaller than that of the O1s peak of bare SiO_2 (533.5 eV).[23] Similarly, with increasing number of SiO_2 layers, the binding energy of O1s was closer to that of bare SiO_2, also suggesting a decreasing interaction between silica particles and organic pigment particles.

The atomic percentages of C, O, Si, and Cl elements of the surfaces for the silica-coated organic pigment particles were calculated on the basis of the X-ray survey at the takeoff angles of 90° and are summarized in Table 2. Just as expected, the Si atomic percentage increased but the Cl atomic percentage decreased with increasing number of SiO_2 layers on the organic pigment particles, suggesting that organic pigment particles were covered more completely under higher numbers of SiO_2 layers adsorbed. The Cl atomic percentage in PE_6–$3SiO_2$ was slightly lower than that of PE_6-2SiO_2, indicating that two SiO_2 layers adsorbed was enough to form a dense silica coat for completely covering the organic pigment particles. The third layer of SiO_2 only increased the thickness of the SiO_2 coat but contributed very little to the coverage ratio.

Porosity and Pore Size. The surface areas of the original organic pigment particles and the silica-coated organic pigment particles were determined by the BET method and are listed in Table 3. It was found that the surface area of organic pigments increased when they were coated by nano-SiO_2 particles. Moreover, the surface area increased as the

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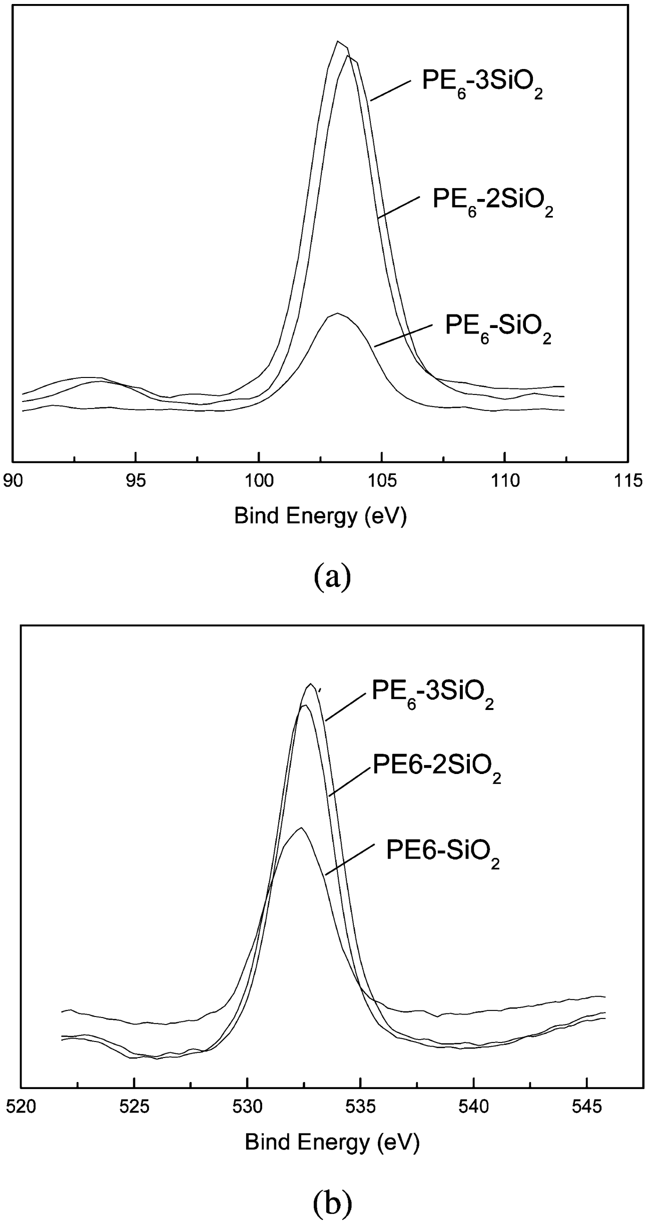

Figure 10. XPS surveys of Si2p (a) and O1s (b) of the silica-coated organic pigment.

Table 2. Surface Atomic Composition of the Silica-Coated Organic Pigment Particles

sample	atomic content (%)			
	C	O	Si	Cl
PE$_6$−SiO$_2$	66.4	23.8	2.7	7.11
PE$_6$−2SiO$_2$	45.9	41.0	11.1	2.0
PE$_6$−3SiO$_2$	41.6	44.5	12.11	1.9

Table 3. Surface Areas of the Silica-Coated Organic Pigment Particles

sample	BET area (m^2/g)	sample	BET area (m^2/g)
original	26.3	PE$_6$−2SiO$_2$	72.3
PE$_6$−SiO$_2$	28.7	PE$_6$−3SiO$_2$	94.1

number of SiO$_2$ layers increased, which should be a result of the porous structure of the silica coats, just observed by TEM.

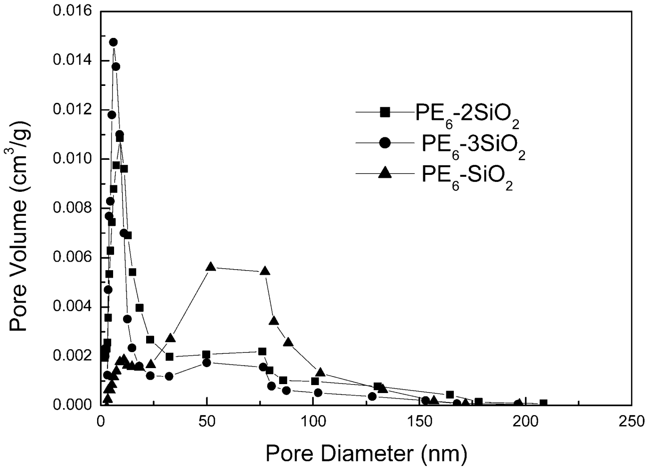

Figure 11. Pore size distribution of the silica-coated organic pigment.

Figure 11 displays the pore size distribution of silica-coated organic pigment particles. When only one layer of SiO$_2$ was coated on the organic pigment particles, a broad pore size distribution from around 40 to 80 nm was observed. But when the second layer of silica was coated, the peak with a broad pore size distribution disappeared and a narrow peak with an average pore size of 5 nm was observed. Moreover, the pore size distribution almost did not change when the third layer of silica was adsorbed, further confirming that the second layer of SiO$_2$ could fully fill the pores in the first silica layer, which was consistent with the results of XPS.

UV−Vis Absorption Spectra. Figure 12a illustrates the UV−vis diffuse reflectance spectra of the polyelectrolyte-precoated organic pigment and silica-coated organic pigment with different silica layers. Since the spectra were determined in the powder state in the diffuse reflectance mode, they should denote the absorbing and scattering properties of the pigment. The lower the diffuse reflection absorption coefficient *F*(*R*), the higher the scattering properties the organic pigment, indicating a decreasing absorbance property. For the polyelectrolyte-precoated organic pigment, there was an obvious absorbance band below 270 nm. This absorbance band decreased remarkably when the organic pigment particles were coated with two and three layers of SiO$_2$, indicating that the nano-SiO$_2$ particles on the surfaces of the organic particles could obviously scatter the UV light, especially below 270 nm wavelength. Figure 12b further indicates the decrease in the UV absorbance peak was attributed to the scattering of nano-SiO$_2$ particles, not to the absorption of nano-SiO$_2$ particles. Either way, this scattering undoubtedly availed to protect the organic pigment from the decomposition induced by ultraviolet light. In other words, silica-coated organic pigments should be expected to have higher durability than uncoated organic pigments.

Figure 12b further shows the UV−vis absorption spectra of polyelectrolyte-precoated organic pigment and silica-coated organic pigment particles with different silica layers. Since the spectra were determined in an aqueous dispersion in transmission mode, they should reflect the absorbance property. Comparing the relative peak areas in Figure 12b indicated no obvious absorbance in the UV range and visible range in comparison with the original organic pigment. The whole shift toward low absorbance should be caused by the decreasing pigment content in the silica-coated organic pigment. This further confirms that the decrease in UV

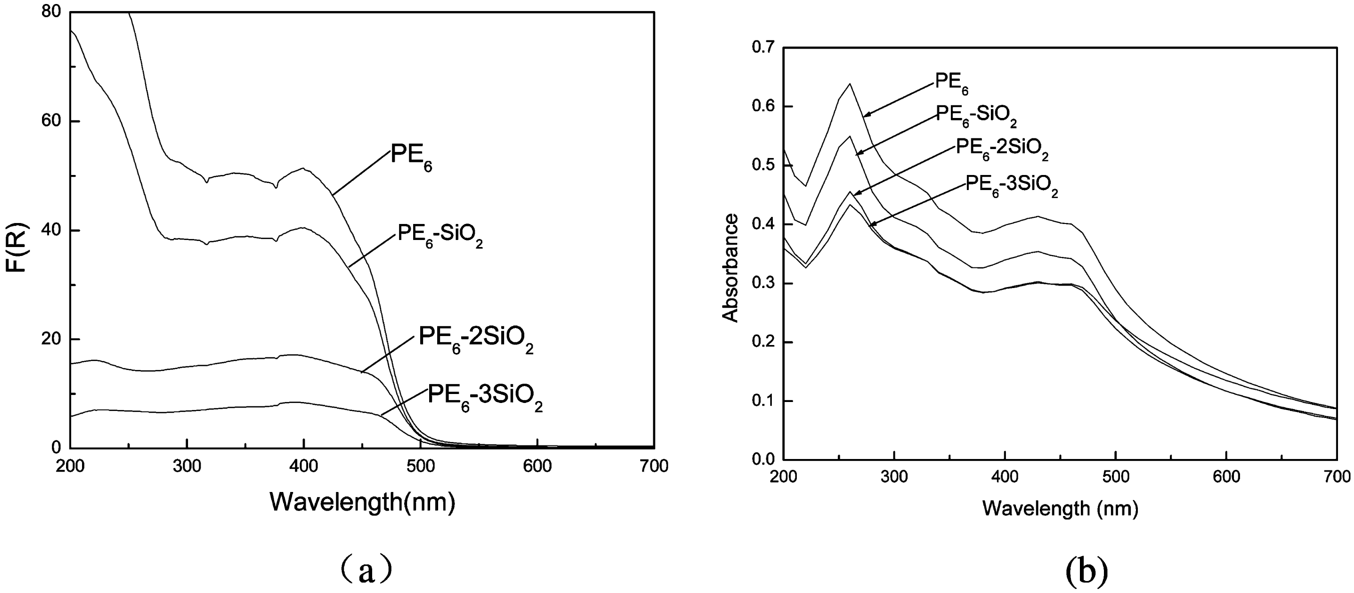

Figure 12. UV−vis spectra of polyelectrolyte-coated organic pigment and silica-coated organic pigment particles with different silica layers (a) in the diffuse reflectance mode and (b) in the transmission mode.

absorbance intensity in Figure 12a resulted from the scattering property of nano-SiO$_2$ particles. Moreover, the colloidal nano-silica particle layer could not decrease the color appearance of the organic pigment, which was very important for its actual application.

Conclusions

This study demonstrates that the organic pigments could be successfully coated by nano-silica particles via the layer-by-layer assembly technique. Two kinds of polyelectolytes (PDADMAC and PSS) were first sequentially adsorbed onto the surfaces of the organic pigment and then coated by nano-SiO$_2$/PGADMAC layer assembly. The silica coverage degree of the organic pigment surface could be remarkably enhanced by increasing the number of polyelectrolyte layers precoating the surfaces of the organic pigment. But excess numbers of polyelectrolyte layers (e.g., ≥8 layers) did not further increase the silica content adsorbed onto the surfaces of the organic pigment. The nano-SiO$_2$ layer assembly also obviously increased the silica content on the pigment. The first layer of nano-SiO$_2$ assembly could markedly increase the particle size of the coated pigment, resulting in relatively rough surfaces, and obvious increases in shell thickness and pore size distribution. But the second and third layers of nano-SiO$_2$ assembly trended to locate at the pores first, causing relatively smooth surfaces, slight increases in shell thickness and surface atomic composition, and a narrow pore size distribution. The silica shell thickness and the morphology of the coated organic pigment could be easily tuned by adjusting the numbers of polyelectrolyte layer and nano-SiO$_2$ layer assemblies. The coated nano-SiO$_2$ particles could considerably improve the UV scattering property of the organic pigment especially after the second and third layers of nano-SiO$_2$ assembly, which should enhance the weather durability of the organic pigment. Also, the coated nano-SiO$_2$ particles could enhance the dispersion ability of the organic pigment in waterborne systems.

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