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The properties of organic pigment encapsulated with nano-silica via layer-by-layer assembly technique

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Abstract

In this paper, an organic pigment was coated with nano-silica particles via layer-by-layer self-assembly technique and some properties were investigated. The results revealed that the coating of nano-silica on the surfaces of pigments could improve the thermal stability, wettability, acid and alkali resistance, and weatherability of the organic pigment.

Keywords: Organic pigment; Nano-silica; Wettability; Weatherability; Acid and alkali resistance

1. Introduction

Organic pigments have been extensively used in coatings, inks and plastics industries or even in color filters [1] for electronics and communication apparatus since they have many advantages such as good photosensitivity, hue, brilliance, color strength, transparence and so on. However, the limited hiding power, poor dispersion ability, and especially the poor weathering durability are the obvious 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. [2] encapsulated an organic phthalocyanine blue pigment into polystyrene latex particles using a miniemulsion polymerization technique to improve its dispersion ability in aqueous system; Fei et al. [3] 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 [4] 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 be also straightly coated with silica film as a protective shell by water glass process to improve the UV shielding property, stability, heat resistance, etc. [5—7]. Recently, we successfully coated the organic pigments with colloidal silica and titania using multi-step layer-by-layer self-assembly technique and sol—gel process, respectively [8—10].

In the present work, we further investigated some properties of the organic pigment particles coated with nano-silica particles via multi-step layer-by-layer self-assembly technique. Benzidine yellow G was applied as the representative of organic pigments since this pigment has good color strength, good transparency, and low cost and is widely used in various types of printing inks while the poor light fastness and weatherability limit its applications in coatings, rubbers and plastics [11]. Several different sizes of nano-silica particles (5 nm, 10 nm and 20 nm) were encapsulated on the surfaces of the organic pigment particles. The results showed that coating of nano-silica particles on the surfaces of the organic pigment could improve the thermal stability, wettability, acid and alkali resistance and weatherability obviously.

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2. Experimental

2.1. Materials

Polyelectrolytes, poly(diallyldimethylammonium chloride) (PDADMAC, Mw < 200 000) and poly(sodium 4-styrenesulfonate) (PSS, Mw = 70 000), were obtained from Aldrich. Sodium chloride (A.R. Grade) was purchased from Shanghai Chemical Reagent Co., Ltd. of China. Deionized water was prepared in our lab. Silica aqueous sol (20 nm, pH = 9.5, solid content = 26.4 wt.%) was obtained from Zhejiang Yuda Chemical Industry Co., Ltd. of China. Silica aqueous sols (10 nm, pH = 8.5–9.5, solid content = 31.6 wt.% and 5 nm, pH = 8.5–9.0, solid content = 15.6 wt.%) were obtained from Jiangyin Guolian Chemical Industry Co., Ltd. of China. Organic pigment, benzidine yellow G (*Pigment Yellow 12*) whose chemical structure is shown in Chart 1, was supplied by Taiwan Hou Chi Chemical Co., Ltd.

2.2. Preparation of nano-silica coated organic pigment

2.2.1. The dispersion of benzidine yellow G

A certain amount of PSS and 100 g of water were charged into a 500 mL plastic beaker and stirred at room temperature for about 10 min to prepare PSS solution, followed by charging with 10 g of organic pigment and then milled for about 1 h on a bead miller with 1 mm ZrO_2 bead as milling medium at a stirring speed of 3500 rpm to obtain stable organic pigment paste with PSS as a dispersing agent.

2.2.2. 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-silica particles and PDADMAC. The detailed preparation procedure is described as follows. Firstly, the superfluous PSS in the organic pigment paste was removed through four cycles of centrifugation and deionized water washing. The obtained paste 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). Secondly, PDADMAC and PSS were subsequently and alternatively deposited onto the surfaces of the PSS coated organic pigment by adding 1 g L^{-1} of aqueous polyelectrolyte solution (containing 0.3 M NaCl). After 20 min adsorption, excess polyelectrolytes were removed by four cycles of centrifugation (15 000 rpm, 15 min) and deionized water washing and then redispersed into deionized water. On repeating the above steps, polyelectrolyte multilayer could form on the surfaces of organic pigment particles according to the experimental demand. The layers could provide a uniformly charged surface which facilitated subsequent nanoparticle adsorption [12–14]. The outermost surface layer was always PDADMAC, thus making the coated particles positively charged. Thirdly, nano-SiO_2 particles were adsorbed onto the surfaces of 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, then the excess nano-SiO_2 particles were removed by four cycles of repeated centrifugation and deionized water dispersion. The electrostatic interaction between the negatively charged silica nanoparticles and the positive PDADMAC was utilized to build up the nanocomposite multilayer. On repeating PDADMAC/SiO_2 deposition via layer-by-layer self-assembly steps, multilayer SiO_2 shell could be obtained. The silica coated organic pigments were designated as PE_i–$jSiO_2$, in which i denotes the layer numbers of polyelectrolytes and j the layer numbers of nano-SiO_2.

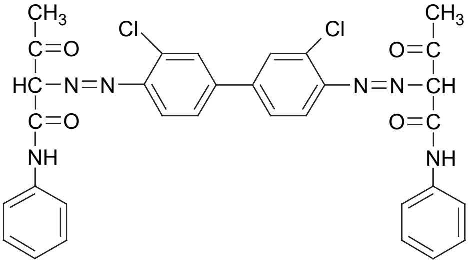

Chart 1. Chemical structure of C.I. Pigment Yellow 12.

2.3. Characterization

2.3.1. The amount of silica adsorbed onto the surfaces of organic pigment

The amount of nano-SiO_2 adsorbed onto 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.

2.3.2. Morphology of the silica coated organic pigment

The morphologies of silica coated organic pigments were observed by transmission electron microscope (TEM Hitachi H-600) and scanning electron microscope (SEM Philips XL30). The samples for TEM observation were sonicated in water for 5 min and deposited onto carbon-coated copper mesh and allowed to air-dry before examination. For SEM observation, the silica coated organic pigments were firstly diluted, then dried on cover glass and finally sputter-coated with gold prior to examination.

2.3.3. BET analysis

The nitrogen adsorption measurements were performed at 77 K using an ASAP 2010 analyzer utilizing Barrett–Emmett–Teller (BET) method for calculation of surface areas and Broekhoff-de Boer (BdB) model was used to calculate the pore size distributions [15].

2.3.4. Wettability of nano-silica coated organic pigment

Contact angles of the organic pigment powder were measured by an optical contact angle measurement system (OCA 15 plus, Dataphysics Company, Germany). The organic pigment powders were pressed with pressing machine to form organic pigment slices. The contact angles of the slices were determined with deionized water as the liquid medium. All the contact angles presented here were the mean of five replicates.

2.3.5. Acid and alkali resistance of nano-silica coated organic pigments

The acid and alkali resistant properties of the organic pigment were determined according to the Chinese National Standard: GB5211.6-85 and GB5211.7-5, respectively. The experimental process is described as follows: 0.5 g of organic pigment powders was added into 20 mL of 2 wt.% HCl solution for acid resistance testing or 20 mL of 2 wt.% NaOH solution for alkali resistance testing followed by shaking in oscillator for a certain time. The acid and alkali resistant abilities of the nano-silica coated pigment could be judged based on the change in color of the filtrates and filtrated pigment powder.

2.3.6. Weatherability of nano-silica coated organic pigment

Accelerated weathering tester (QUV/Se, UVA-340 nm light, American Q-Panel Company) and hand ultraviolet ray examination lamp (ZF-7C, UVA-254 nm light, Shanghai Gucun Electron Optic Instrument Factory) were used to measure

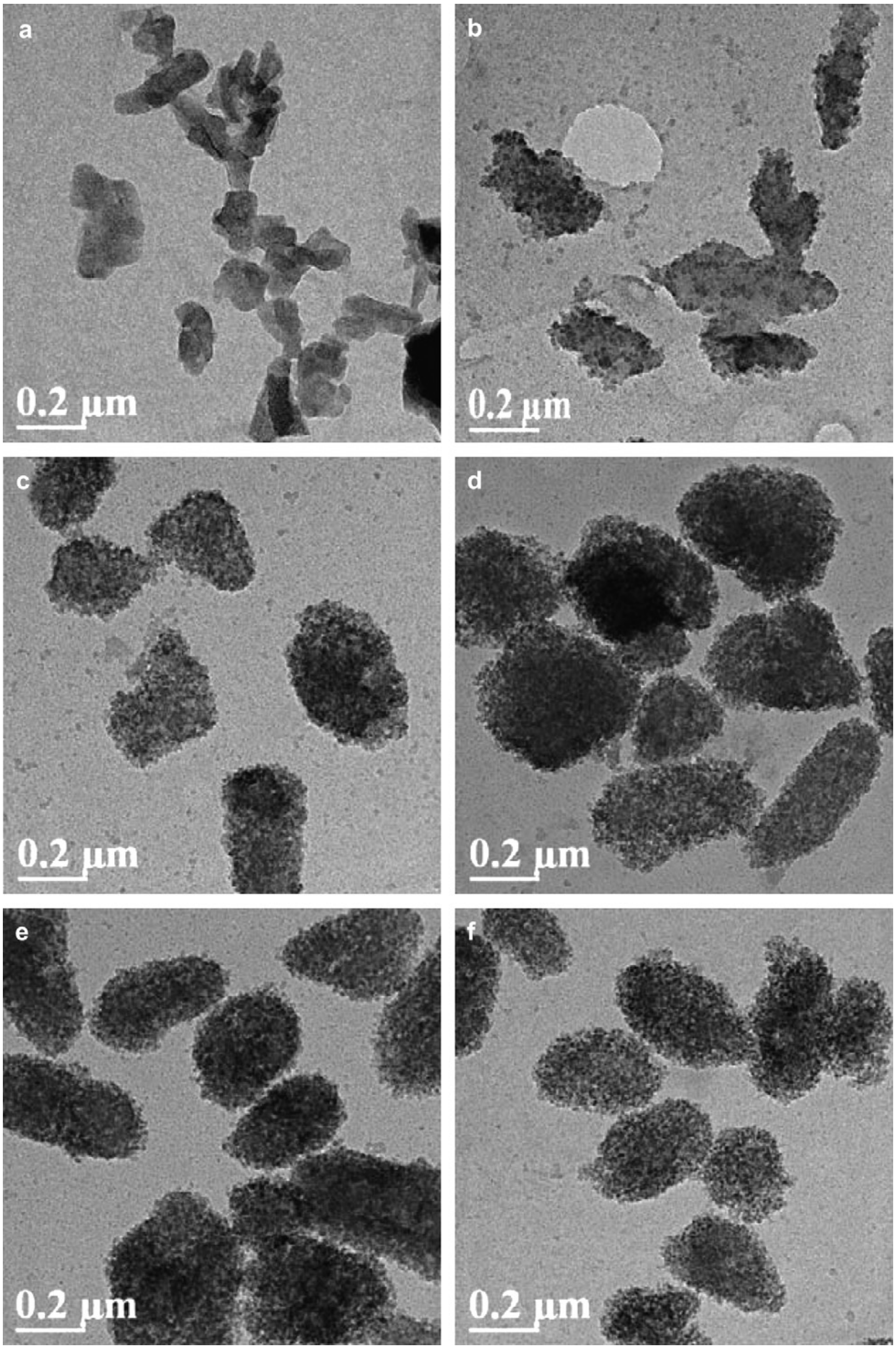

Fig. 1. TEM images of original C.I. Pigment Yellow 12 (a); PE_6-SiO_2-20 nm coated benzidine yellow G (b); PE_6-2SiO_2-20 nm coated benzidine yellow G (c); PE_6-3SiO_2-20 nm coated benzidine yellow G (d); PE_6-3SiO_2-10 nm coated benzidine yellow G (e); PE_6-3SiO_2-5 nm coated benzidine yellow G (f).

the weatherability of the modified organic pigment. The original pigment and the modified pigment were introduced into latex coating in a typical formulation. The coatings were cast on panels and dried at room temperature, and then irradiated under 340 nm or 254 nm UV ray for some period of time, respectively. The color difference of the coating panels was measured by X-rite SP64 portable sphere spectrophotometer.

3. Results and discussion

3.1. Morphology of the nano-silica coated organic pigment

The TEM images of the organic pigment coated with different layers and particle sizes of nano-silica are demonstrated in Fig. 1. Compared with original benzidine yellow G (Fig. 1a), nano-silica particles were obviously found on the surface of the organic pigment particles, and the mean particle size of the organic pigment increased with both the layer numbers (see Fig. 1b–d) and the particle sizes (see Fig. 1d–f) of nano-silica. This could be also observed by the SEM images as shown in Fig. 2. By further observing the morphologies of the original pigment and the modified pigment, it could be found that the original pigments were poorly dispersed, indicating the severe aggregation of pigment particles as shown in Figs. 1a and 2a. However, the dispersing property was improved obviously after nano-silica particles were coated, and the more the nano-silica layers were coated, the better was the dispersing property observed.

3.2. Porosity and pore size

The specific surface areas of the original pigment particles and the nano-silica coated pigment particles were determined by BET and Langmuir methods, as summarized in Table 1. It was found that the specific surface areas of the pigment particles

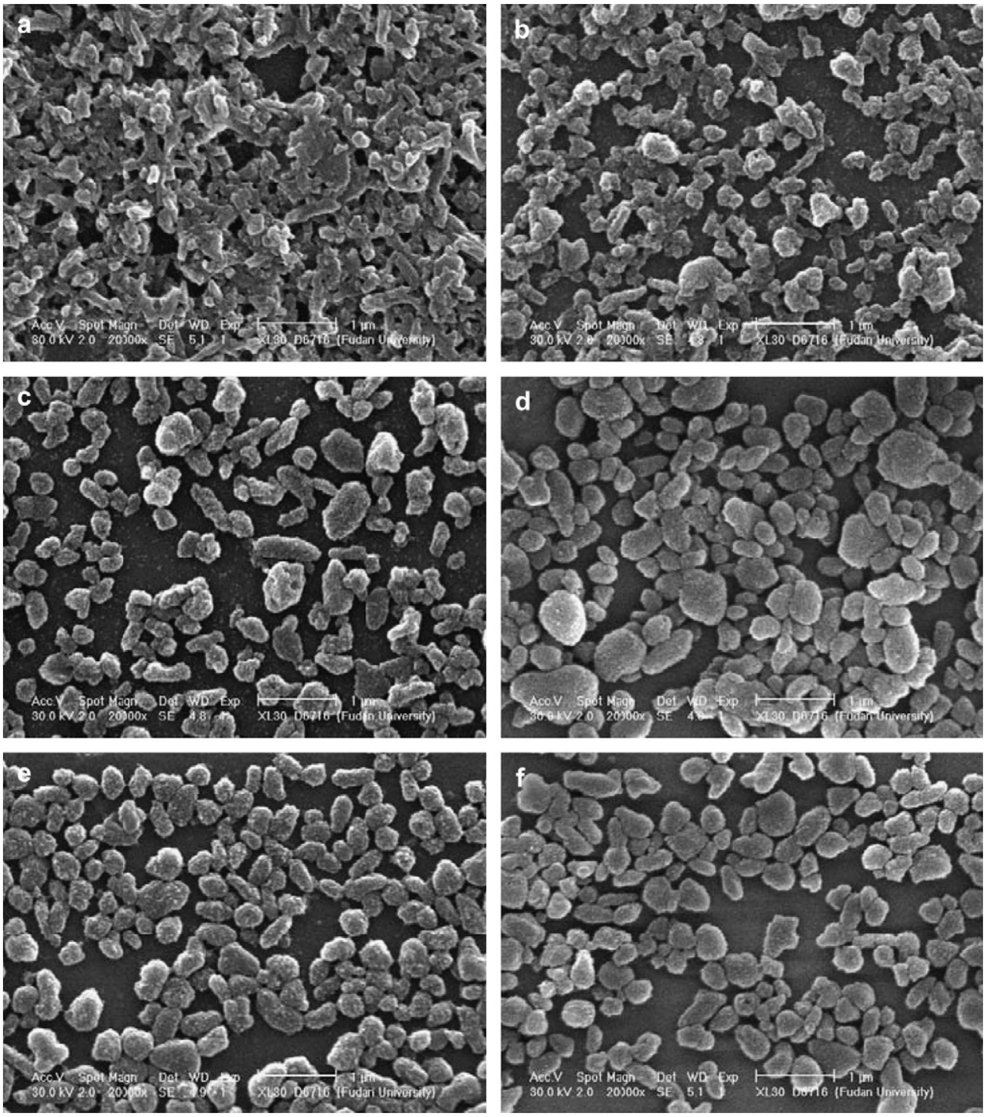

Fig. 2. SEM images of original benzidine yellow G (a); PE_6-SiO_2-20 nm coated benzidine yellow G (b); PE_6-2SiO_2-20 nm coated benzidine yellow G (c); PE_6-3SiO_2-20 nm coated benzidine yellow G (d); PE_6-3SiO_2-10 nm coated benzidine yellow G (e); PE_6-3SiO_2-5 nm coated benzidine yellow G (f).

Table 1
The specific surface areas of original pigment and nano-silica coated pigment

Samples	BET surface area (m^2/g)	Langmuir surface area (m^2/g)
Benzidine yellow G	43.9	56.2
PE_6–$3SiO_2$-20 nm	58.5	74.5
PE_6–$3SiO_2$-10 nm	56.5	72.0
PE_6–$3SiO_2$-5 nm	53.9	68.5

increased distinctively when they were coated with nano-silica, but the nano-silica with different particle sizes seemed to have no impact on the specific surface areas, which were similar to the nano-silica coated organic pigment yellow 109 [8].

Fig. 3 presented the N_2 adsorption/desorption isotherms of the nano-silica coated organic pigment particles. When the relative pressure P/P^0 was less than 0.8, the slopes of all the curves were very small, indicating very little amount of small size pores existing on the surfaces of organic pigment particles. When the relative pressure P/P^0 was more than 0.8, the slopes of the curves increased sharply. Moreover, a slight separation between the adsorption isotherms and desorption isotherms of the original pigment was observed which should be the evidence of a small quantity of micropores existing on the organic pigment surfaces. A remarkable separation between the adsorption isotherms and desorption isotherms of other samples was obtained, which should be the evidence of large quantities of micropores existing on the different particle sizes of nano-silica coated pigment particles [16].

Fig. 4 displays the pore size distribution of the original pigment particles and the nano-silica coated pigment particles. Compared with original pigment, all the samples coated with nano-silica had more pore size distribution from about 20 nm to 50 nm, nevertheless, different nano-silica coated pigments had almost the same pore size distribution.

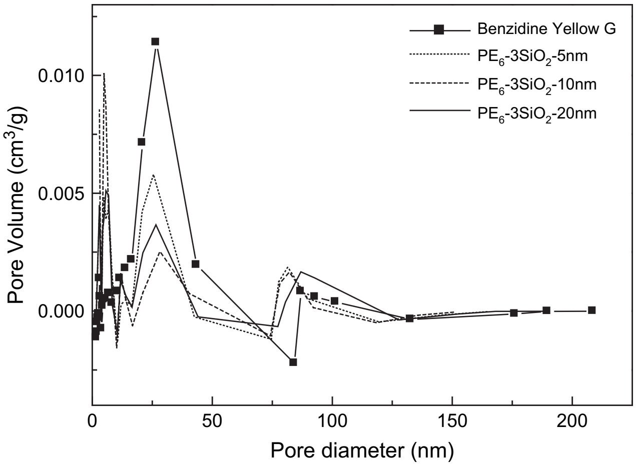

Fig. 4. The pore size distribution of original pigment and nano-silica coated pigment.

3.3. Thermal stability

Fig. 5 illustrates the differential TGA curves of the original pigment and nano-silica coated pigment. Two weight loss stages were observed for original pigments: one was in the range of 200–380 °C and another was in the range of 450–600 °C, both resulting from the decomposition of the pigment.

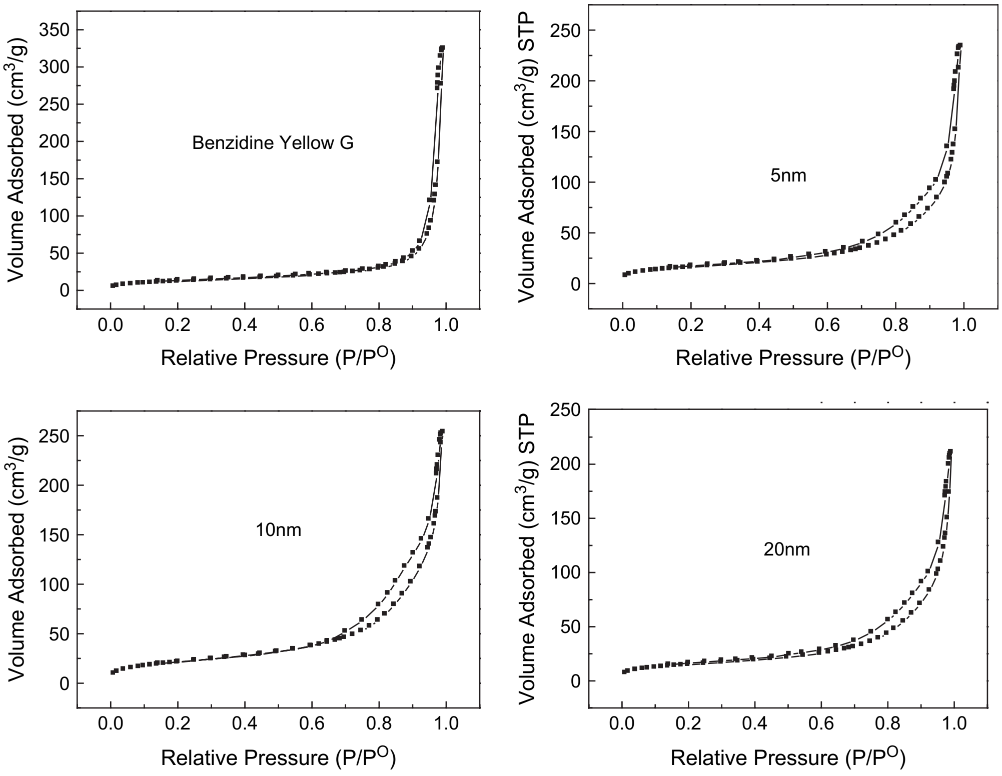

Fig. 3. Nitrogen adsorption/desorption isotherm of original pigment and nano-silica coated pigment.

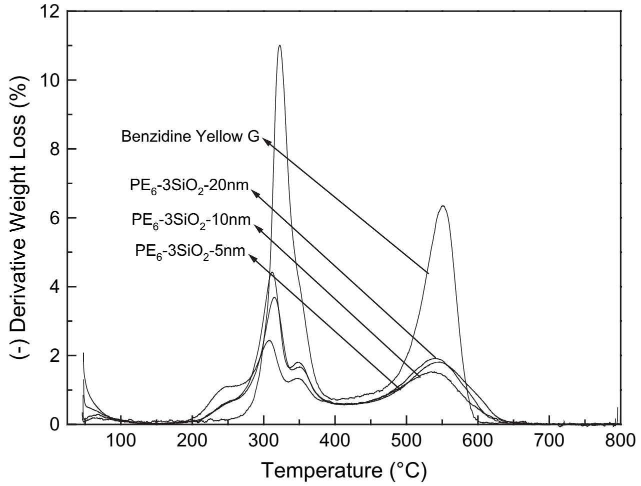

Fig. 5. DTG curves of the original pigment and the nano-silica coated pigment.

For the nano-silica coated organic pigments, there were also two weight loss stages observed. The onset decomposition temperatures of these nano-silica coated pigments were almost the same as that of the original pigment, suggesting that the coating of nano-silica on the surfaces of pigments could not postpone the onset decomposition temperature. However, the encapsulation of nano-silica on the surfaces of pigment caused lower and wider weight loss peaks than the original pigment, suggesting that the coating of nano-silica could depress the decomposition rate of organic pigment, increasing the thermal stability of the original pigment. But different particle sizes of nano-silica almost had no influence on the thermal stability of the organic pigment.

3.4. Wettability of the nano-silica coated pigment

Since nano-silica particles are hydrophilic, the nano-silica coated pigment should have enhanced wettability. Table 2 shows the contact angles of water on the original pigment and nano-silica coated pigment. Just as expected, coating of nano-silica could decrease the contact angle of water on the modified pigment, no matter which nano-silica was employed, suggesting that coating of nano-silica on the surfaces of organic pigment could improve the dispersing property of the latter in water-borne system.

Table 2
The contact angles of the original pigment and the nano-silica coated pigment powder

Samples	Contact angle (°)	
	Beginning	After 2 min
Benzidine yellow G	73.5	70.2
PE$_6$–SiO$_2$-20 nm	53.2	23.2
PE$_6$–2SiO$_2$-20 nm	28.6	0
PE$_6$–3SiO$_2$-20 nm	22.6	0
PE$_6$–3SiO$_2$-10 nm	19.5	0
PE$_6$–3SiO$_2$-5 nm	18.3	0

3.5. Acid and alkali resistance properties

Fig. 6 presents the pictures of the filtrates of the original pigment and the nano-silica coated pigment immersed in 2 wt.% HCl solution and 2 wt.% NaOH solution, respectively. The tube numbers and the color difference (ΔE) are listed in Table 3.

From both the color change in Fig. 6 and the color difference data in Table 3, it could be seen that the filtrates of the silica coated pigment had considerably lower color and color difference than the original pigment, indicating that the encapsulation of nano-silica on the surfaces of organic pigment could improve the acid and alkali resistance properties of the latter obviously.

3.6. Weatherability

The original pigment and the nano-silica coated pigment were introduced into latex coatings according to the typical formulation for the preparation of coating panels. The coating

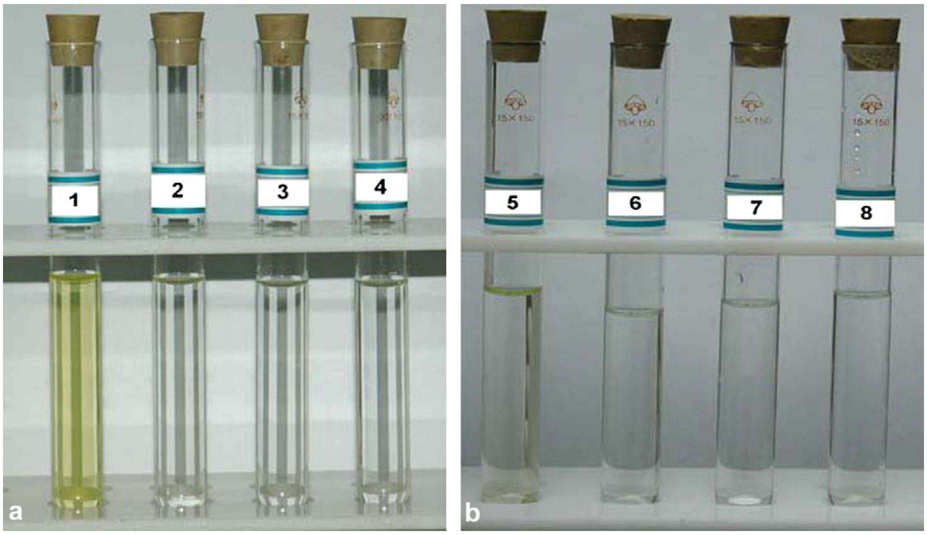

Fig. 6. Color change of the filtrates of original pigment and the modified pigment: after immersing in acid solution (a); after immersing in alkali solution (b).

Table 3
Color difference of the original pigment and the modified pigment after immersing in 2% acid solution and 2% alkali solution

Tube no.	Samples	ΔE	
		Acid resistance	Alkali resistance
1, 5	Benzidine yellow G	4.0	4.5
2, 6	PE_6-3SiO_2-20 nm	1.7	1.2
3, 7	PE_6-3SiO_2-10 nm	2.3	1.5
4, 8	PE_6-3SiO_2-5 nm	2.0	1.5

Table 4
The color difference of latex coatings before and after irradiation

Samples	ΔE			
	1 wt.% (340 nm)	5 wt.% (340 nm)	1 wt.% (254 nm)	5 wt.% (254 nm)
Benzidine yellow G	12.5	12.9	4.0	16.7
PE_6-3SiO_2-20 nm	10.5	13.0	1.3	8.0
PE_6-3SiO_2-10 nm	12.0	11.0	1.8	8.3
PE_6-3SiO_2-5 nm	9.1	12.9	1.3	6.2

panels were exposed under 340 nm UV ray for 500 h or 254 nm UV ray for 150 h. Table 4 presents the color difference of these coatings before and after UV irradiation. When exposed under 340 nm ray, the coatings with the nano-silica coated pigment had a comparable color difference to the coating with the original pigment, indicating that the nano-silica coating was not strong for shielding 340 nm UV ray. However, when exposed under 254 nm ray, the coatings embedded with the nano-silica coated pigment had considerably lower color difference than the coating with original pigment, indicating that the coating of nano-silica on the pigment surfaces could shield 254 nm UV ray effectively. This was consistent with the nano-silica particle-coated organic pigment itself [8], which had an obvious absorbance band below 270 nm, indicating that nano-silica had UV absorbance in UVC and not in UVB and UVA regions. But different particle-size nano-silica seemed to have little influence on the shielding of 254 nm UV ray.

4. Conclusions

In this study, benzidine yellow G was used as the representative of organic pigment and coated by nano-silica particles using layer-by-layer self-assembly technique. Electronic images and contact angles indicated that encapsulation of nano-silica on the pigment surfaces could improve the dispersibility of organic pigment in water-borne system obviously. TGA results illustrated that nano-silica coating could depress the decomposition rate of organic pigment. Immersion experiments showed that nano-silica coating also enhanced the acid and alkali resistance performances of the organic pigment. Ageing test revealed that encapsulation of nano-silica on the surfaces of the pigment could shield 254 nm UV ray remarkably.

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