Preparation of Nanoscale TiO_2-eencapsulated C.I. Pigment Blue 15:3 via Sol-Gel Method

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Abstract

A nanoscale TiO_2-encapsulated C.I. pigment blue 15:3 was prepared through sol-gel method. The effects of encapsulation conditions on particle size were investigated in detail. Transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), contact angle analysis (CAA) and zeta potentials of TiO_2-encapsulated C.I. pigment blue 15:3 at different pH value proved that encapsulation layer of TiO_2 was formed on C.I. pigment blue 15:3 surface. The dispersion with small particle size was obtained when the mass ratio of octadecyl amine polyoxyethylene ether amine 2-quaternary ammonium salt (OPA) to pigment was 25%, the mass ratio of butyl titanate (BT) to pigment was lower than 11%, the dropping rate of BT was 3 mL/min and the pH value was 5.8. The encapsulated phthalocyanine blue pigment had enhanced stabilities to centrifugal force and freeze-thaw treatment.

INTRODUCTION

Organic pigments are an important group of colorants that have been extensively used in coating, printing and paint industries due to its advantages in color strength and transparency. However, the limited hiding power, large particle size, poor dispersion stability, and especially the poor weather and light durability are obviously obstacles limited those organic pigments in many applications [1]. It is urgent and necessary to overcome these drawbacks using effective methods.

Surface coating of nanoscale organic pigment with the other materials to design core-shell structures is currently an effective method to overcome the shortcomings that mentioned above. Surface modification has the possibility to tailor the physical and chemical properties of core materials depending on the nature of the shell [2–5]. At present, several methods have been developed to encapsulate organic pigment using polymeric materials, such as emulsion or mini-emulsion polymerization [6-14], phase separation [15, 16], in situ polymerization [17, 18]. Encapsulation organic pigment with inorganic materials can improve the wettability and light durability of organic pigment. Sol-gel is a common method to prepare the hybird prticles with core-shell structure. For example, Lin produced monodisperse, spherical and nonaggregated pigment particles with a core/shell structure using sol–gel process [19]. Zhou prepared SiO_2/PS/TiO_2 core-shell hybrid microspheres via miniemulsion polymerization and sol-gel method [20]. Sathiyamoorthy synthesized core-shell particles containing chloroaluminiumphthalocyanine using a sol-gel technique [19]. Supplit investigated the process of aluminum pigments that coated by sol-gel method [20]. To improve the thickness of the encapsulated layer, Yuan applied the layer-by-layer assembly to encapsulate the organic pigment particles with colloidal nano-silica particles [1].

Although, many researches reported pigment moderfication using sol-gel method, few reports were involved in preparing the encapsulated organic pigment with nanoscale particles. In this study, we demonstrated a sol-gel method to prepare the nanoscale TiO_2-encapsulated C.I. pigment blue 15:3, the properties of TiO_2-encapsulated pigment and its dispersion have been investigated in detail.

EXPERIMENTAL

Materials

Butyl titanate (BT, AR) was supplied by Guoyao Chemical Company, Shanghai, China. HCl, NaOH, ethanol (AR) was purchased from Shanghai Chemical Reagent Co., Ltd, China. Octadecyl amine polyoxyethylene ether amine 2-quaternary ammonium salt (OPA, its chemical structure was shown in chart 1) was supplied by Suzhou Sunmun Science and Technology Co., Ltd, China. C.I. pigment 15:3 was supplied by Changzhou North American Company, China.

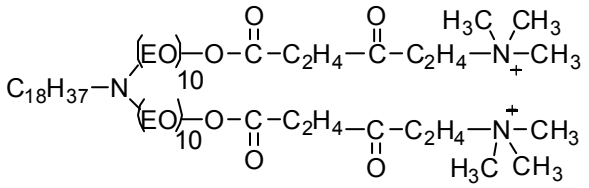

Chart 1 *the chemical structure of OPA*

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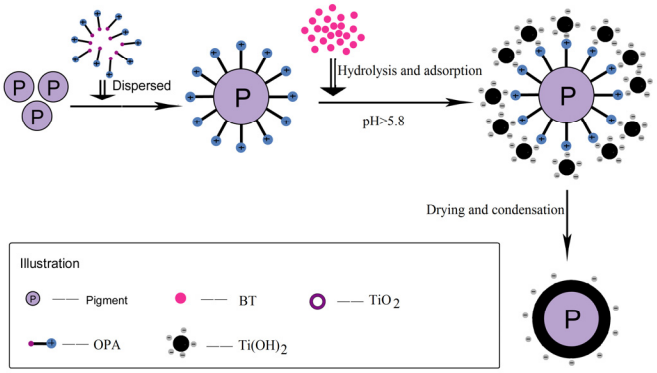
30 g C.I. pigment blue 15:3 was added into water solution with 170 g OPA under stirring at 500 r/min. The pH value was adjusted to 9 using NaOH solution (0.1 mol/L). The mixture was transferred to a bead mill (Minizeta 03E, Netzsu, Germany) using ZrO_2 bead (0.8 mm, mass ratio of ZrO_2 to pigment 5:1) as milling media. The mixture was dispersed for 2 h to obtain the nanoscale pigment dispersion. The prepared dispersion was centrifuged at 13000 r/min to get the OPA-modified C.I. pigment blue 15:3.

The process for encapsulation of C.I. pigment blue 15:3 by sol-gel method was depicted in Scheme 1. 20 g OPA-modified C.I. pigment blue 15:3 was placed in a beaker which contained a certain amount of distilled water and 100 g ethanol. The mixture was treated with ultrasonic wave for 30 min, and then transferred

to a 4-neck flask equipped with stirrer, thermometer and condenser. 50 g BT ethanol solution was dropped into the flask under stirring at 1500 r/min. After that, the dispersion was stirred for 3 h at 35 °C to get the dispersion. Finally, the prepared dispersion was centrifuged at 5000 r/min to get the slurry. The slurry was washed with ethanol for 3 time and then dried to get the TiO_2-encapsulated C.I. pigment blue 15:3. 5 g TiO_2-encapsulated C.I. pigment blue 15:3 was dispersed into 95 g distilled water and then stirred for 30 min to get the TiO_2-encapsulated C.I. pigment blue 15:3 dispersion.



Scheme 1. *process for encapsulation of C.I. pigment blue 15:3 by sol-gel method*

Characterization

Particle size: the particle size was determined by dynamic light scattering (DLS) using a Malvern Zetasizer Nano ZS90 instrument (Malvern Instruments Co., Ltd, England) at 25 °C with a fixed angle of 90 °. The cumulate analysis was used in analyzing the DLS data of all the samples. Each sample was measured for three times, the particle size was reported as an average value.

Zeta potentials: The Zeta potentials of the dispersion which diluted to 100 times by distilled water were measured by Nano-ZS90. Each sample was measured for three times, the Zeta potentials were reported as an average value.

Fourier transforms infrared spectroscopy (FTIR): FTIR spectra of samples (in KBr pellet) were recorded on a Nicolet Nexus 560 FTIR spectrometer.

Transmission electron microscopy (TEM): One drop of the dispersion was diluted 4000 times with distilled water and placed on a 400-mesh carbon-coated copper grid and dried in air. The morphology of pigment particles was observed on a JEM-100SX transmission electron microscope.

Contact angle analysis (CAA): The samples were uniformly put onto a glass slide, and then pressed with another a glass slide to ensure a flat surface. One drop of the distilled water dropped onto the samples, after balanced for 30s, and the contact angle of the sample to distilled water was recorded by Krüss DSA 100.

Freeze-thaw Stability: The sample was sealed and stored at -5 °C for 24 h, and then put into an oven at 60 °C for another 24 h. The particle size distribution was measured by DLS method, and the freeze-thaw stability was evaluated using the changes of the particle size distribution.

Centrifugal stability: The sample was centrifuged at 2000 r/min for 30 min. The particle size distribution was measured by DLS method, and the stability to centrifugal forces was evaluated using the changes of the particle size distribution.

RESULTS AND DISCUSSION

Preparation of TiO_2-encapsulated C.I. pigment blue 15:3

Figure 1a show that particle size of the dispersion decreases first and then increases with increasing the amount of OPA, and reaches the minimum when mass ratio of OPA to C.I. pigment blue 15:3 is 25%. The C.I. pigment blue 15:3 can not be fully occupied when amount of OPA is low, thus the uncoated C.I. pigment blue 15:3 will be attracted via van der waals forces. However, when amount of OPA is high enough, multi-layer adsorption of OPA onto C.I. pigment blue 15:3 surface will be formed, which also leads to a large particle size.

Amount of BT can also affect the particle size of TiO_2 encapsulated C.I. pigment blue 15:3. Figure 1b shows that the particle size of TiO_2 encapsulated C.I. pigment blue 15:3 increases as the amount of BT increases. It may be due to that the more amount of BT is loaded, the thicker encapsulated layer onto the C.I. pigment blue 15:3 particles will be formed, which leads to large particle size.

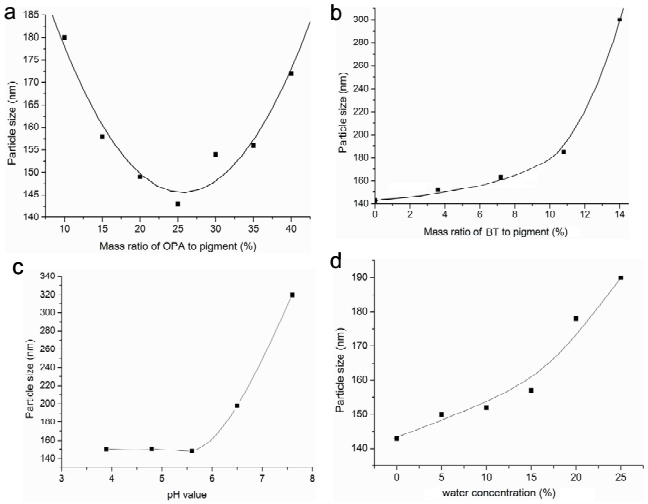


Figure 1 *Effect a) amount of OPA, b) amount of BT, c) pH value and d) ffect of water conc on particle size of TiO2-encapsulated C.I. pigment blue 15:3 dispersion*

pH value can affect the electric forces among TiO_2 and OPA-modified C.I. pigment blue 15:3, and therefore influence the particle size of TiO_2 encapsulated C.I. pigment blue 15:3. Figure 1c shows that the particle size changes small with an increase of pH value from 3.80 to 5.65, and increases greatly when pH value is higher than 5.65. TiO_2 will bring some positive charges when pH value is lower than the isoelectric point of TiO_2. Therefore, it can not encapsulate C.I. pigment blue 15:3 for the electric repulsive forces, thus the particle size changed small with an increase of pH value. However, when pH value is higher than the isoelectric point of TiO_2, TiO_2 will take some negative charges, and thus it can successfully encapsulate the C.I. pigment blue 15:3 for the electric attraction forces.

The water concentration of the solution can also affect the particle size of TiO_2-encapsulated C.I. pigment blue 15:3 since the water influences on hydrolysis and condensation of BT during the sol-gel process. Figure 1d shows that the particle size of TiO_2-encapsulated C.I. pigment blue 15:3 increases slightly when water concentration is lower than 15%, and improved sharply when water concentration is higher than 15%. The high water concentration is, the more amount of TiO_2 is produced which was used to encapsulate the pigment particles. Therefore, the particle size increases as the water concentration increases. However, when water concentration is high enough, the uncompleted encapsulation layer will be formed for the high hydrolysis rate of BT, thus the stability of the dispersion will be destroyed and thus leads to a large particle size.

Character of the TiO_2-encapsulated C.I. pigment blue 15:3

TEM

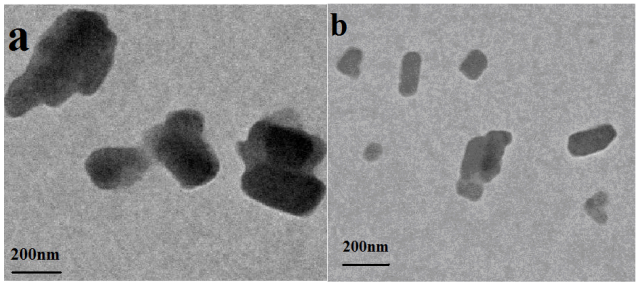


Figure 2. *TEM photos of (a) original C.I. pigment blue 15:3 and (b) TiO_2-encapsulated C.I. pigment blue 15:3*

The morphology of TiO_2-encapsulated and original C.I. pigment blue 15:3 is shown in Figure 2. It is clearly seen that the particles of TiO_2-encapsulated C.I. pigment blue 15:3 is smaller and more uniform than original pigment. The results indicated that the dispersing ability of C.I. pigment blue 15:3 is improved when it was encapsulated by TiO_2.

Contact angle

Figure 3 show that TiO_2-encapsulated C.I. pigment blue 15:3 has an improved wettability. Compared to the water contact angle of 107.78 ° of the original C.I. pigment blue 15:3, the TiO_2-encapsulated C.I. pigment blue 15:3 has a water contact angle of 56.45 °. The reason is that the C.I. pigment blue 15:3 surface was introduced in more hydrophilic after TiO_2 encapsulation.

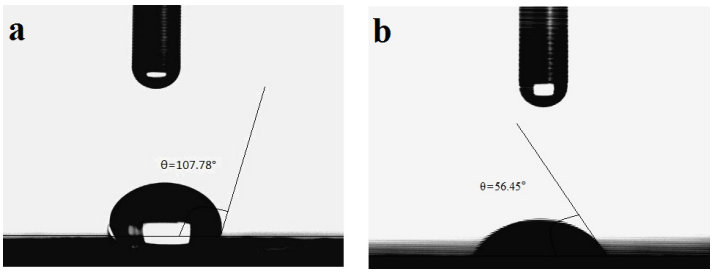


Figure 3. *Water contact angles of (a) original C.I. pigment blue 15:3 and (b) TiO_2-encapsulated C.I. pigment blue 15:3*

Zeta potentials

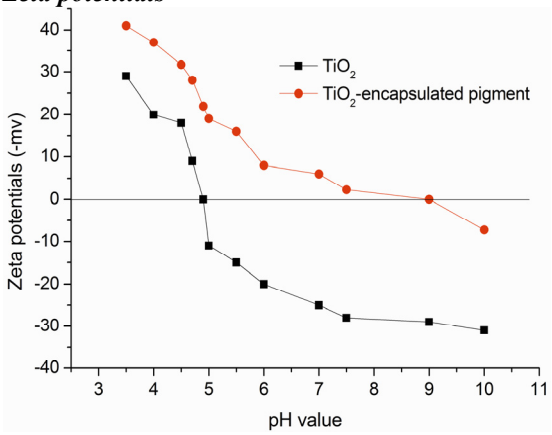


Figure 4. *Zeta potentials of TiO_2 and TiO_2-encapsulated C.I. pigment blue 15:3 at different pH value*

Figure 4 shows the Zeta potentials of TiO_2 and TiO_2-encapsulated C.I. pigment blue 15:3 at different pH value. Just as similar to TiO_2, the TiO_2-encapsulated C.I. pigment blue 15:3 also has an isoelectric point, and its isoelectric point is moved to high pH value. The reason may be attributed to that some positive charges onto the pigment particles are introduced by OPA. These results also indicate that some amounts of TiO_2 are encapsulated the C.I. pigment blue 15:3 particles.

Stability of TiO_2-encapsulated C.I. pigment blue 15:3 dispersion

Figure 5 show that the particle size distribution of TiO_2-encapsulated C.I. pigment blue 15:3 dispersion changes little when it was treated under freeze-thaw treatment or centrifugal force. It is known that some charges will introduce onto TiO_2-encapsulated C.I. pigment blue 15:3 and then produce large repulsive forces, leading to an excellent stability. Theses results also indicate that TiO_2 encapsulated C.I. pigment blue 15:3 dispersion had an outstanding stability.

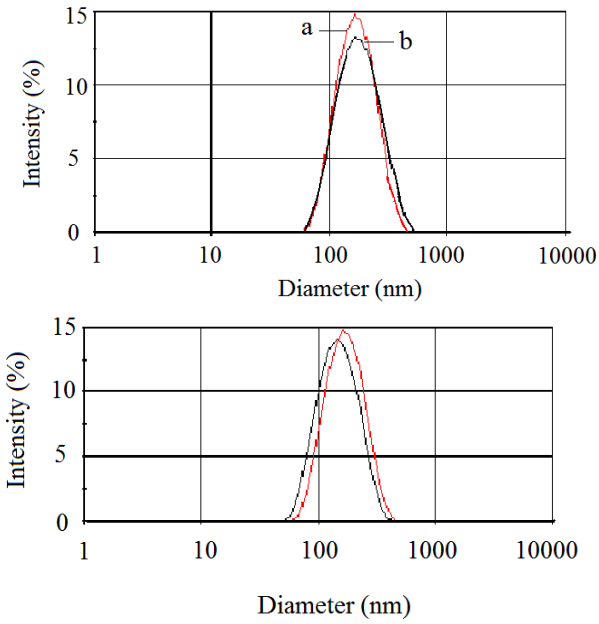


Figure 5. *Particle size distribution (up) a) TiO_2-encapsulated C.I. pigment blue 15:3 dispersion after freeze-thaw treatment and b) TiO_2-encapsulated C.I. pigment blue 15:3 dispersion; (down) a) TiO_2-encapsulated C.I. pigment blue 15:3 dispersion after centrifugal treatment and b) TiO_2-encapsulated C.I. pigment blue 15:3 dispersion*

CONCLUSIONS

A nanoscale TiO_2 encapsulated C.I. pigment blue 15:3 dispersion can be prepared by sol-gel method. The dispersion with small particle size is obtained when the mass ratio of octadecyl amine polyoxyethylene ether amine 2-quaternary ammonium salt to pigment is 25%, the mass ratio of butyl titanate (BT) to pigment is lower than 11%, the dropping rate of BT is 3 mL/min and the pH value is 5.8. The encapsulated phthalocyanine blue pigment has enhanced stabilities to centrifugal force and freeze-thaw treatment.

Acknowledgements

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Author Biography

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