

Preparation and Characterization Core-Shell Particles and Application for E-Ink

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Received 2 May 2006; accepted 2 November 2006

DOI 10.1002/app.25815

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: the core-shell particles were prepared by dispersion copolymerization. The core-shell particles were characterized with Fourier-transform infrared spectroscopy, Transmission electron microscope and scanning electron microscope. The dispersion stability and electrophoretic performance of core-shell particles were studied in the mixed medium of tetrachloroethylene and cyclohexance. Microcapsules containing the core-shell particles

were prepared by coacervation. Results showed that the core-shell particles had good dispersion stability and it had no electric response, which could be used as grounding particles for E-Ink. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1195–1199, 2007

Key words: core-shell particles; copolymerization; microcapsules; E-Ink

INTRODUCTION

Electronic ink display, which is made of the microcapsules, including electrophoretic particles and fluid medium, has recently been of great interest due to its advantages with in-on-paper, high reflectance, good contrast ratio, wide-viewing angle, image bistability, and low power consumption.^{1–3}

According to the number of electrophoretic particles in the microcapsules, E-Ink divided into two type display methods. One is “single particle display,” the other is “dual particles display.”⁴ Among them, because suspending fluid is colored by dyes in “single particle display”, some color of dyes may be incorporated in the electrophoretic particles to influence display quality. Comparing to “single particle display,” “dual particles display” solved the earlier problem, but during operation of an electrophoretic display, positive and negative charged particles can become agglomeration under the influence of an electric field because of attraction of positive and negative charge. To solve this problem, the uncharged particle was designed as a grounding particle. TiO₂ has a good optical contrast with other particles so that it can be useful as grounding particle. However, TiO₂ has a density about 4.0 g/cm³, which is too high to match with any organic liquid to prevent the sedimentation problem. Therefore, encapsulation TiO₂ using a polymeric materials is a key process to fabricate the grounding particle.

In recent years, a new encapsulation technology has been developed, in which the inorganic particles in polar system is coated by dispersion polymerization.^{5–7} Dispersion polymerization is characterized with the fact that the monomer and the initiator are soluble and the polymer insoluble in the reaction medium.⁸ In the article, we prepared core-shell particles by dispersion copolymerization, as shown in Figure 1. And we studied its dispersion stability and electrophoretic performance in the mixture medium of tetrachloroethylene and cyclohexance. To study electrophoretic performance of core-shell particles in microcapsules, we prepared microcapsules containing the core-shell particles by coacervation.

EXPERIMENTAL

Materials

Titanium dioxide (TiO₂, rutile, Nanjing Haitai Nanometer Materials, China) pigment powder with an average diameter of 30 nm was used. Methacryloyl-propyltrimethoxysilicane (SB570) coupling agent was purchased from Tianjin Shengbin Chemical Engineering (China) and used as received. Styrene (St), divinylbenzene (DVB), 2,2'-azobis(2-methylpropionitrile) (AIBN), and polyvinylpyrrolidone (PVP, $M_w = 30,000$ g/mol) (Tianjin chemical Reagent) were analytical pure grade. Tetrachloroethylene, cyclohexance, acacia, gelatin, acetic acid, glutaraldehyde, sodium carboxy methylcellulose, sodium hydroxide (NaOH), toluene, ethanol (Tianjin Kewei, China) were analytical pure grade.

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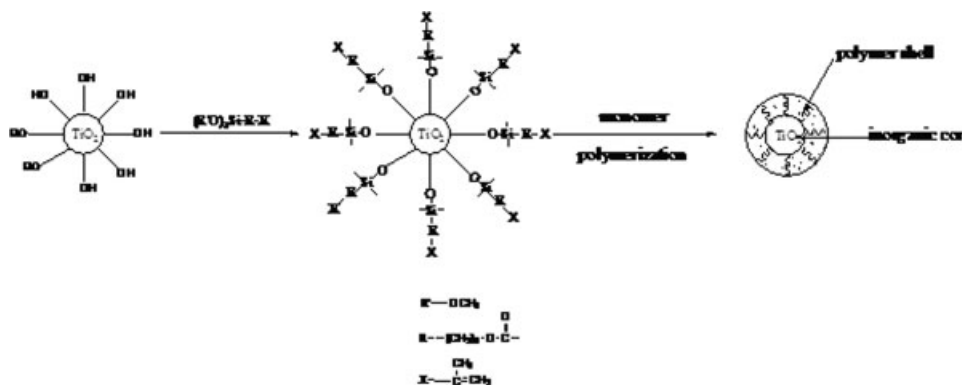


Figure 1 Schematic representation of preparation of core-shell particles.

Preparation of core-shell particles

About 1.00 g nano-TiO₂ particles were dispersed in 160 mL toluene with dissolving 0.10 g SB570, the mixture was stirred at 120°C in nitrogen atmosphere. SB570-TiO₂ was isolated by filtration, washed many times with ethanol to remove excess SB570 and finally dried at room temperature, SB570-TiO₂ was obtained.

About 2.00 g PVP as a stabilizer was dissolved in 100 mL ethanol, then 3.00 g St and 3.00 g DVB were added, 1.47 g SB570-TiO₂ particles were dispersed in the earlier system by sonification for 15 min at room temperature. The mixture was poured into a 250 mL four-necks round bottomed flask equipped with a mechanical stirrer, a thermometer, a reflux condenser and a nitrogen gas inlet and outlet, and 0.30 g AIBN was added into reactor. The stirring speed was fixed with 250 rpm. The polymerization was carried out at 70°C for 6 h in a nitrogen atmosphere. The products were isolated from the mixture by filtration, washed with ethanol three times, and then extracted with toluene. Finally, the product was dried at room temperature.

Experimental techniques

Fourier-transform infrared spectra of the samples in the range 400–4000 cm⁻¹ were made with a fully computerized BID-RAD FIS3000 spectrometer. Measurements were performed in the transmission made in KBr pellets.

Transmission electron micrographs were recorded under vacuum by using JEOL-100CX-II. The micrographs were acquired after drying the samples at 100 k multiple.

Scanning electron micrographs were recorded by using PHILIPS XL-30 ESEM. The micrographs were acquired after coating samples with gold at 20 keV.

Dispersion stability was characterized according to sedimentation percentage. The dispersion liquids were prepared by dispersing a solid content 3 wt %

of tetrachloroethylene and cyclohexane ($V_t : V_c = 1 : 1.4$). The dispersion liquids were placed for 80 h at room temperature. The volume of the upper clear liquid and liquid, including solid were recorded. The formula of the sedimentation percentage was as follows:

$$T = \frac{V_0}{V_0 + V_c}$$

where T is the sedimentation percentage, V_c , the volume of the upper clear liquid, V_0 , the volume of liquid containing solid.

Electrophoretic performance was measured by a JS94J Micro-electrophoretic apparatus.

Encapsulation by coacervation

About 0.1 g core-shell particles were dispersed in 10 mL the mixed medium of tetrachloroethylene and cyclohexane ($V_t : V_c = 1 : 1.4$) by sonification for 1 h at room temperature. 1.00 g of acacia was dissolved in 100.00 g of water with stirring at 50°C for 30 min, then, 1.00 g of gelatin was carefully added over about 20 s to avoid lumps. The resulting solution was then stirred for 20 min. With agitation at 800 rpm, 5 mL the mixed immiscible fluid, prepared as described earlier, was introduced into the aqueous phase. The resulting fluid/water emulsion was allowed to emulsify for 20 min. Agitation was then reduced to 200 rpm. The pH was then reduced till 4.4 over 5 min with a 10% acetic acid solution, the contents of the reactor were slowly cooled to 10°C. When the solution temperature reached 10°C, 3.00 mL of a 37% formalin solution was added, and the solution was further stirred for another 60 min, 0.40 g of sodium carboxymethylcellulose was added, and the pH was then raised to 8–9 by the addition of a 10 wt % solution of NaOH. The thermostat bath was then set to 50°C, and allowed to stir for another 60 min. Finally, the precipitated microcapsules were washed with water many times. Transmission micro-

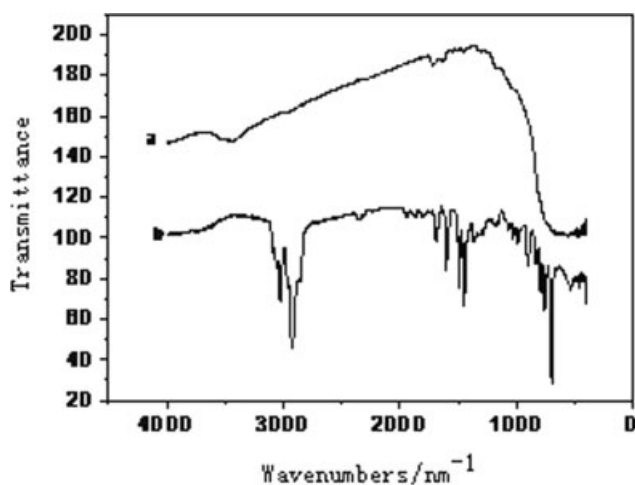


Figure 2 Fourier-transform infrared spectra of (a) SB570-TiO₂, (b) core-shell particles.

scope images of the microcapsules in the presence of either electric field or not electric field were recorded on a 53-XC Transmission microscope.

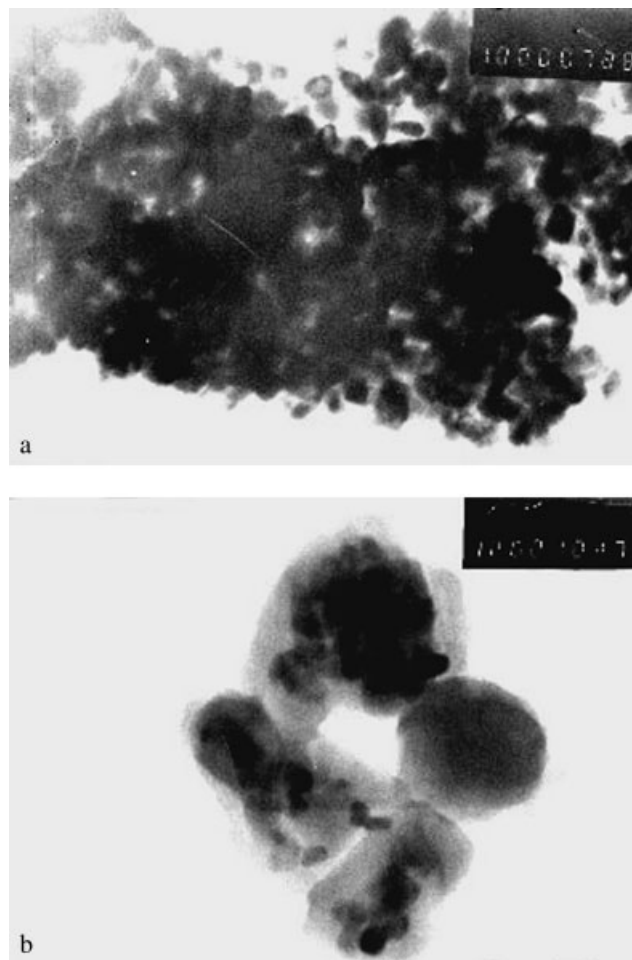


Figure 3 TEM of (a) SB570-TiO₂, (b) core-shell particles.

RESULTS AND DISCUSSION

Fourier transform infrared spectra

FTIR spectra results of the samples were shown in Figure 2. Figure 2(a) corresponds to SB570-TiO₂, (b) to core-shell particles.

In the Figure 2(a), it existed the broad peak below 800 cm⁻¹, which was characteristic of Ti—O—Ti backbone. But in the Figure 2(b), this broad peak below 800 cm⁻¹ vanished, it was observed the characteristic peaks at about 1400–1600cm⁻¹ belonged to C=C bands of the phenyl ring. The bands in region 2800–3100cm⁻¹ were corresponding to the CH₂ and CH₃ groups of polymer backbone. It could be indicated that SB570-TiO₂ was encapsulated by the copolymer of St and DVB completely.

Transmission electron microscope

The transmission electron micrographs of SB570-TiO₂ and the core-shell particles were shown in Figure 3. Figure 3(a) was corresponding to SB570-TiO₂, (b) to the core-shell particles.

With regard to SB570-TiO₂ particles morphology, it could be seen that SB570-TiO₂ particles were encapsulated by P(St-co-DVB).

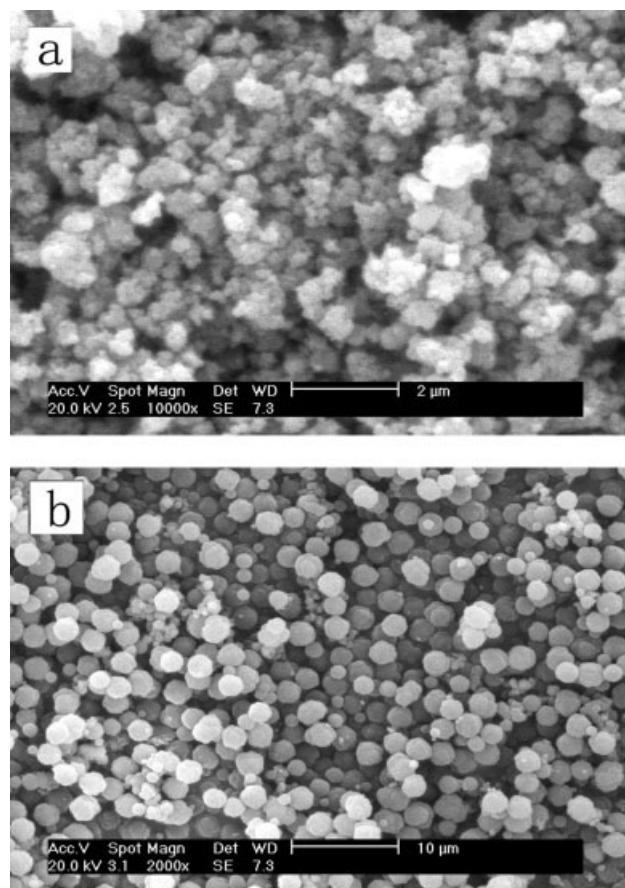


Figure 4 SEM of (a) SB570-TiO₂, (b) core-shell particles.

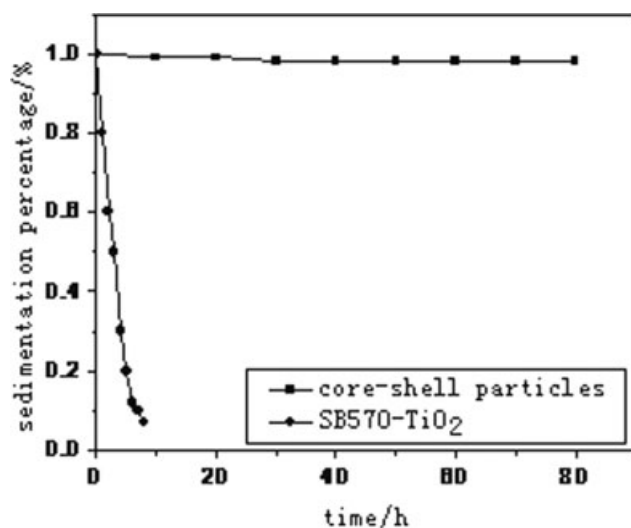


Figure 5 Dispersibility curve of particles in the mixed medium of tetrachlorethylene and cyclohexane.

Scanning electron microscope

SEM of SB570-TiO₂ and core-shell particles were shown in Figure 4.

Figure 4 showed clearly that the difference between SB570-TiO₂ and core-shell particles. The shape of SB570-TiO₂ was not sphere, the particle diameter of SB570-TiO₂ was in the range of 400–600nm. Comparing to Figure 4(a) of SB570-TiO₂, Figure 4(b) showed that the core-shell particles had uniform particle size distribution, which were in the range of 2–3 μm . Combining the results of TEM, it was deduced

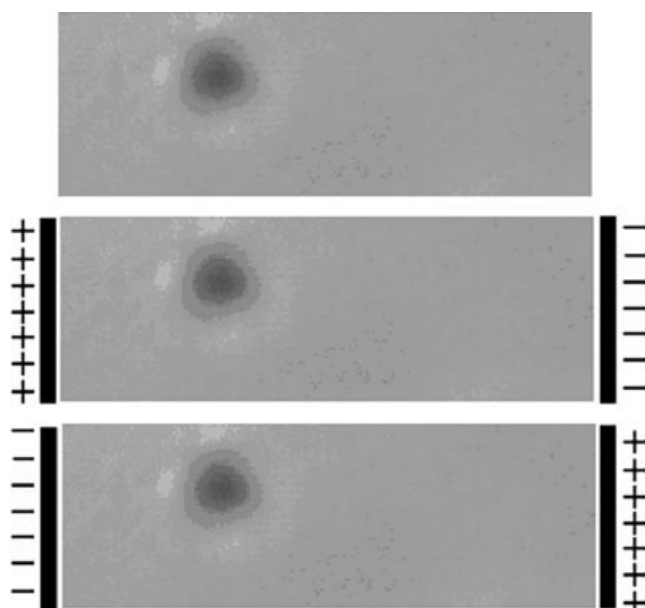


Figure 6 Electrophoretic performance of the core-shell particles in the mixed medium.

TABLE I
The Electrophoretic Mobility of Particles

Sample	Shell thickness (nm)	$\mu/(\text{cm}^2 \text{ V s})$
TiO ₂	0	0.001788
SB570-TiO ₂	0	0.02674
Core-shell particles	5	0
	10	0
	50	0
	100	0

that many SB570-TiO₂ were encapsulated in a core-shell particles.

Dispersibility and electrophoretic performance study

Figures 5 and 6 showed that dispersibility and electrophoretic performance of SB570-TiO₂ and core-shell particles in the mixed medium of tetrachlorethylene and cyclohexane, respectively.

From the Figure 5, it could be conclude that the core-shell particles had a good dispersion stability in the mixed medium of tetrachlorethylene and cyclohexane,. On the contrary, SB570-TiO₂ deposit in the mixed medium quickly. It indicated that encapsulation decreased SB570-TiO₂ density to match with the dispersion medium. In addition, from the Figure 6, the core-shell particles did not move under the electric field. The reason for this was the shielding effect of the P(St-co-DVB) shell. As shown in Table I, it could be seen that TiO₂ had weak negative charge in the mixed medium of tetrachlorethylene and cyclohexane because of the interaction of π bond of tetrachlorethylene and TiO₂ surface hydroxyl groups. According to Lykleme,⁹ π bond of tetrachlorethylene could attract hydrogen ion of TiO₂ surface hydroxyl groups to form the negative charge. After modification with SB570, the electrophoretic mobility of SB570-TiO₂ increased due to the change of the TiO₂ surface property. The hydrophilic surface of

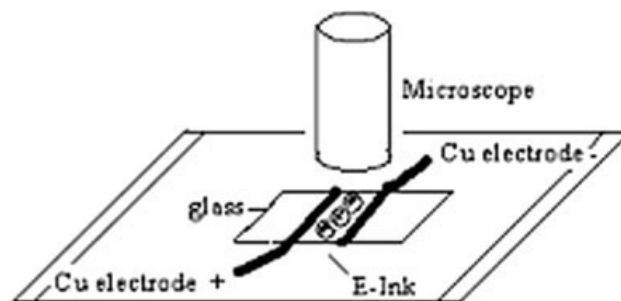


Figure 7 Device for checking the electric response of E-Ink.

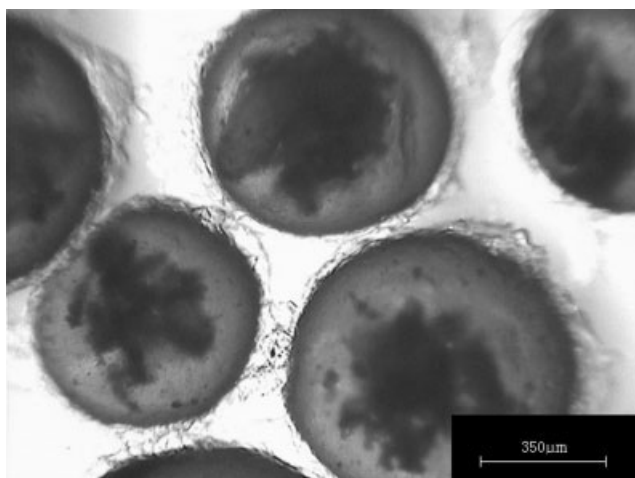


Figure 8 Encapsulation of the core-shell particles.

TiO₂ limited interaction of π bond of tetrachloroethylene and TiO₂ surface hydroxyl groups, on the contrary, the hydrophilic surface of SB570-TiO₂ provided the opportunity for this interaction. When encapsulation of SB570-TiO₂ with P(St-co-DVB) shell, the core-shell particles had not any charge. The main reason was that P(St-co-DVB) shell prevented this interaction. From Table I, the 5 nm shell made the core-shell particles had not any charge, which indicated the shielding effect of the P(St-co-DVB) shell was strong.

Encapsulation

To investigate the movement of core-shell particles in the microcapsules, we had made a device for checking the electric response of E-Ink., as shown in Figure 7. After a single layer microcapsules were placed between two Cu-electrodes, the direct current electric field was applied by two Cu-electrodes.

On the basis of these results earlier, the core-shell particles, as materials of microcapsules core, were encapsulated by coacervation, as shown in Figure 8.

Figure 8 showed that the core-shell particles were distributed in the center of the microcapsules. When the DC electric field ($E = 75$ V/mm), the core-shell particles did not move to any side of the microcapsules. From the observation, it suggested that the core-shell particles could be the grounding particle of E-Ink, which was consistent with the results of core-shell particles electrophoretic performance.

CONCLUSIONS

Encapsulation of SB570-TiO₂ particles by the copolymer of St and DVB was achieved by dispersion copolymerization. Comparing to SB570-TiO₂, the core-shell particles had a good dispersion stability in the mixture medium of tetrachloroethylene and cyclohexane. Electrophoretic performance study showed that core-shell particles had no electric response. Microcapsules containing the core-shell particles were prepared by coacervation. Results showed that the core-shell particles could be as grounding particles for E-Ink.

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