Electrophoretic characterization of Hollow Titania Sphere for E-paper display

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Abstract
We report a microcapsule-based electronic ink display technique, containing hollow titania particles which were prepared via a complex coacervation method using gelatin and gum arabic. In order to reduce density mismatch between nanoparticels and dielectric medium, hollow titania particles were introduced. Microcapsules were then prepared using gelatin to improve the elasticity of the microcapsule wall and their electrophoretic characteristics were investigated[1]

1. Introduction

Recently the electronic paper technology has been introduced as one of the most promising method of flexible display. Among several electronic paper techniques[1,2,3] a microcapsule-type electronic ink based on the electrophoresis is to display charged particles in dyed medium as core materials to make the image view due to electrostatic migration of dispersed ink particles. However lack of long-term stability due to the electrophoretic nanoparticle clustering, agglomeration, and lateral migration is regarded to be a major drawback. Meanwhile titanium dioxide (TiO_2) nanoparticles with its whiteness and chemical stability have been used as electrophoretic nanoparticles of electronic paper. However relatively high density (4.28 g/cm^3) of TiO_2 leads to severe sedimentation problem in a suspending medium. To overcome this impediment, a microencapsulation method which is a very useful technique to coat a core material using a wall material has been introduced. Concurrently, in order to lower the high density of TiO_2, many researches have been performed especially with respect to core-shell structure[4,5] by a dispersion polymerization. Core-shell nanoparticles can be prepared by controlled adsorption of inorganic precursors onto the core particles[6]. In this study, as a electrophoretic nanoparticles, we prepared cationic polymeric nanospheres as core materials which are continuously treated with to form organic core-titania shell hybrid nanoparticles. The formation of the organic-inorganic hybrids was achieved by rapid adsorption of titania through the hydrolysis of titania precursors. These particles can further be turned into hollow shells both by calcinations[7-10]. Once the synthesis of hollow nanospheres was complete, the preparation of microcapsules of hollow TiO_2 spheres were followed using a water soluble protein – gelatin and polysaccharide- gum arabic by complex coacervation[11,12]. A complex coacervaton is a phase separation phenomenon caused by the interactions of the oppositely charged polyelectrolytes in aqueous media. Obtained microcapsules show elastic properties and stability about the external impact due to the gelatin. Furthermore the response behavior of hollow-TiO_2 particles in the microcapsules to the electric field was characterized.

2. Experimentals

2.1 Materials

Styrene (99%), butyl acrylate (99+%), [2-(methacryloxy)ethyl] trimethyl ammonium chloride (MOTA, 75 wt%), 2,2'azobis(2-methylpropionamidine) dihydrochloride (AIBA), titanium(Ⅳ) butoxide(97%), poly(vinylpyrrolidone)(PVP, Mw 55,000), oil blue N, gum-arabic and glutardialdehyde (50wt%) were purchased from Aldrich. OLOA 1200 was purchased from Chevron. Isopar G oil was purchased from Exxon Corps. Styrene was purified with NaOH solution to remove a polymerization inhibitor. AIBA was recrystallized from a 50/50 weight water/acetone mixture. Magnesium sulfate (anhydrous), sodium hydroxide (bead), sodium chloride and citric acid were purchased from Samchun chemical. Gelatin A was purchased from DC chemical.

2.2 Preparation of Hollow Titania Nanospheres

Cationic polystyrene was synthesized based on the cationic colloidal particles which were prepared by surfactant-free emulsion copolymerization of styrene and butylacrylate in the presence of a cationic

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comonomer, [2-(methacryloyloxy)ethyl] trimethylammonium chloride (MOTAC) using azobis(isobutylamidine hydrochloride)(AIBA) as an initiator. The polymerization was carried out at 80 °C for 24 hr and stirring speed was adjusted at 700 rpm. The procedure to prepare the cationic colloids, coated with titania precursor consists of two steps: adsorption of poly (vinylpyrrolidone)(PVP) and the growth of the titania shell in ethanol. The cationic polystyrene nanoparticles were placed already in an ethanol solution and a solution of PVP in ethanol was added. Immediately after this a titanium(IV) butoxide ethanolic solution was added under vigorous stirring. During the reaction the charge on the particles was changed from positive to negative. The coated particles were then washed with ethanol and dried in a vaccum oven at 40 °C. Once this process has been completed, synthesized TiO_2-coated polymeric nanoparticles were heated to 500 °C in air to form anatase TiO_2 and to remove the colloidal template, which resulted in hollow nanospheres.

2.3 Preparation of microcapsule

As a dielectric dye solution, Oil Blue N and Isopar G oil was mixtured. Hollow-TiO_2 particles were added to the dye solution with some amounts of OLOA 1200. Nanoparticle suspensions were sonicated using an ultrasonic generator (G2806, Kyungil Ultrasonic Co., Korea) which has a nominal frequency of 28 kHz, with a power of 600 W for about 10 min. Emulsification and coacervation were performed in a 500 mL double-wall reactor. With agitation, the prepared oil suspension was poured into the gelatin aqueous solution at 45 ℃. And then arabic gum solution was added in the solution. The pH of the mixture was adjusted to 4.3 with citric acid to induce the complex coacervation. The temperature of the mixture was lowered to 8 °C. Glutaraldehyde solution was added for crosslinking the gelatin. After 12 hr, the product was washed with deionized water to remove unreacted chemicals.

3. Characteization

The morphology of the particles was analyzed by transmission electron microscope (TEM) and scanning electron microscope (SEM). Electrophoretic mobility of the hollow-TiO_2 particles was investigated via an electrophoretic light scattering apparatus (Photal ELS-8000, Otsuka). Microcapsule images were taken by optical microscopy (Olympus BX51).

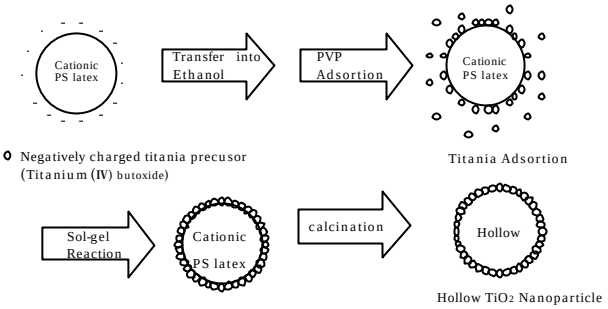

Figure 1. Schematic description of synthesis of hollow titania nanoparticles

4. Results

4.1 Hollow TiO_2 particles

Figure 2 shows TEM images of PS particles, TiO_2 coated PS particles and hollow TiO_2 particles for comparison. The size of PS particles was 160 nm and the thickness of coated TiO_2 on the PS particles surface was 20 ~ 25 nm. After heating the TiO_2 coated PS particles at 500 ℃, the PS cores were removed by calcination and amorphous phase of TiO_2 was changed to anatase crystal. During the calcination process, the size of the hollow TiO_2 particles was decreased about 60 nm. From the zeta potential result, after the coating process, positive charged PS particles change to a negative charge because of the capture of negative charged TiO_2 precursor on the surface of the PS particles. Figure 3 shows the SEM image of hollow titania nanoparticles after being calcined at 500 ℃. Because of thick titania coating, the hollowness of the particles was hardly observed.

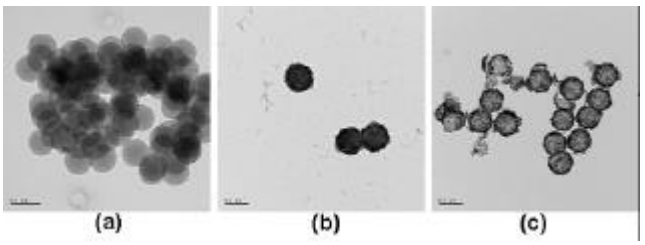

Fig 2. TEM images of PS particles (a), TiO_2 coated PS particles (b), hollow TiO_2 particles (c)

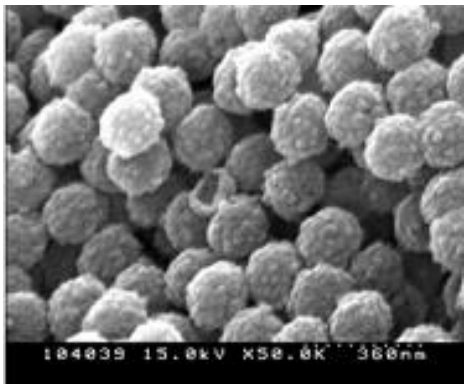

Figure 3. SEM image of hollow TiO_2 particles

4.2 Microcapsules

Figure 4 is an optical microscope image of microcapsules of hollow TiO_2 particles. Microcapsules have elliptical and transparent wall. The black spherical part of the microcapsules is a suspension droplet of dielectric medium and hollow TiO_2 particles. We confirmed that dielectric medium and hollow TiO_2 partilcles are coated with gelatin and gum arabic by complex coacervation. The average size of the microcapsule was about 90 ㎛ and suspension droplet size was about 60 ㎛.

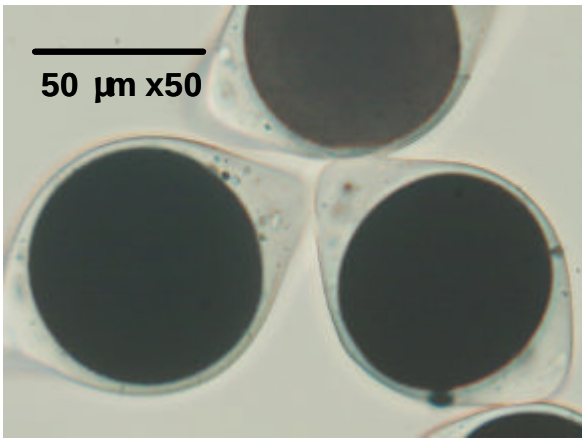

Figure 4. OM image of microcapsules

5. Conclusions

In this study, the nanoparticles with the organic core and the inorganic shell have been synthesized by using stepwise reactions such as the soap-free emulsion copolymerization of the cationic colloidal core and the thermal condensation of the titania shell. After calcinations of the polystyrene core, the hollow TiO_2 nanoparticles were also prepared. Capsules containing the hollow TiO_2 nanoparticles suspensions as the core materials were fabricated with the gelatin aqueous solution and arabic gum aqueous solution as a wall materials by complex coacervation.

6. Acknowledgements

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7. References

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