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Microcapsules by Complex Coacervation for Electronic Ink

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Electrophoretic TiO_2 nanoparticles in a low dielectric medium can be utilized in non-emissive flexible display such as an electronic paper. To prevent the aggregation and to reduce the density of neat TiO_2 nanoparticles, the surface of TiO_2 particles was modified by acrylic copolymer. The surface modified TiO_2 nanoparticles, which were dispersed in low dielectric oils, were encapsulated by the complex coacervation of gelatin and gum Arabic. Then, core-shell type microcapsules were eventually fabricated. The capsules were crosslinked by the reaction between glutaraldehydes and amino groups in gelatinto improve the durability of the microcapsules. These microcapsules were stable during vacuum drying and were easily layered on the surface of the ITO substrates because of their flexibility. A simple electrophoretic display cell was constructed and both the color change and the response time were monitored.

Keywords: complex coacervation; electrophoresis; encapsulation; nanoparticle; titanium dioxide (TiO_2)

INTRODUCTION

Electrophoretic display utilizes the electromigration phenomena of charged nanoparticles, which are dispersed in a low dielectric medium [1,2], and it has advantages such as low power consumption, high contrast and high reflectivity. Electrophoretic nanopaticles are usually microencapsulated to protect the active particles from environment

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or to prevent the aggregation and lateral movement of the particles [2,3], thereby extending the lifetime of the display.

In this study, the surface of rutile TiO_2 nanoparticles was modified by acrylic copolymer to reduce the density of neat TiO_2 as well as to prevent the particle aggregation. Complex coacervation of gelatin and gum Arabic was carried out to form microcapsules [4], which were consisted of the surface modified TiO_2 nanoparticles, low dielectric medium and charge control agent. To enhance the durability of microcapsules, the wall of the capsule was crosslinked by glutaraldehyde. A simple electrophoretic display cell was then fabricated by using ITO coated transparent electrodes with a 210 μm gap, which was filled with the crosslinked microcapsules. When a positive DC electric field (70 V) was applied to the upper electrode, the migration toward the electrode of the modified TiO_2 particles in the microcapsules was observed under an optical microscopy.

EXPERIMENTAL

Preparation of P(MMA-co-EDGMA-co-MAA) Coated TiO_2

TiO_2 (MT 500 B, Tayca Corp.) nanoparticles with the average particle size of 30–50 nm were dispersed in poly(vinyl pyrrolidone) (PVP) solution in methanol by sonication for 1 h at room temperature. For the surface coating of the TiO_2 nanoparticles, methyl methacarylate (MMA) and ethylene glycol dimethylate (EDGMA) were introduced to the TiO_2 dispersion. Then, they were copolymerized on the surface of TiO_2 in the presence of 2,2′-azobisisobutylonitrile (AIBN) as an initiator for 6 h at 60°C under the nitrogen. In order to create charges on the surface of the PMMA coated TiO_2, methylacrylic acid (MAA) was polymerized sequentially for 12 h at 60°C. Finally, poly(MMA-co-EDGMA-co-MAA) coated TiO_2 particles were obtained and they were lyophilized after washing [5].

Preparation of Microcapsules by Complex Coacervation

Core materials including the surface modified TiO_2 particles, charge control agent (OLOA), and a dye were dispersed in the mixture of halocarbon and Isopar-G, and they were emulsified in gelatin (type B, isoelectric point (IEP) = 5.0) [6] solution at 40°C for 150 min. 10 w/w % gum Arabic solution was added to the gelatin emulsion, and warm deionized water (40°C) were slowly dropped to control the colloidal concentration [7,8]. To stabilize the colloids, the pH of the colloidal solution was adjusted to pH 4.0 by citric acid solution. When the mixture was cooled down to 11°C, the shell of gelatin/gum Arabic

surrounding the core materials was solidified and cured by glutaraldehyde. To increase the crosslinking efficiency, the reaction was carried out at 55°C at pH 9.5. Crosslinked microcapsules were washed with deionized water several times and vacuum dried at room temperature. During the purification and drying processes, the microcapsules were stable without breakage.

RESULTS AND DISCUSSION

Figure 1 shows SEM micrographs of both the neat TiO_2 particles and the TiO_2 particles that were modified by the poly(MMA-co-EDGMA-co-MAA) layer. The purpose of the surface modification is

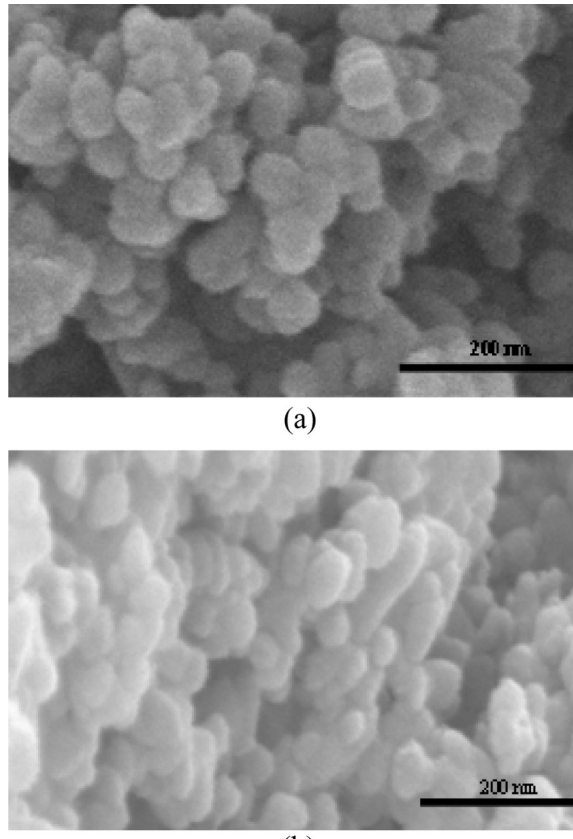


FIGURE 1 SEM micrographs of (a) neat TiO_2 and (b) the surface modified TiO_2 nanoparticles by acrylic copolymers.

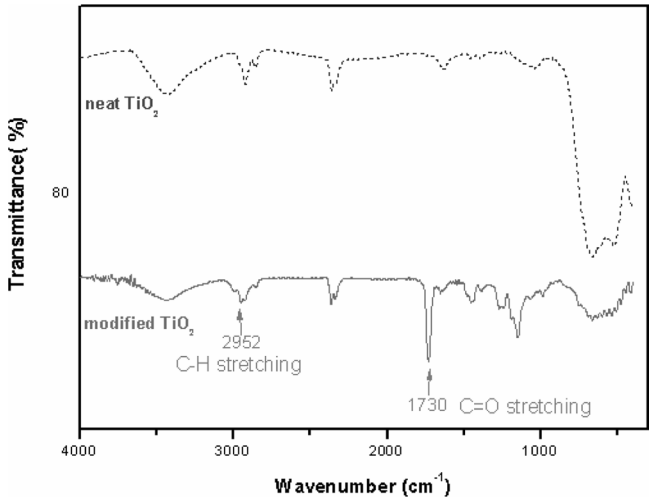


FIGURE 2 FTIR spectra of neat TiO_2 and the surface modified TiO_2 nanoparticles.

two-fold; to lower the density of the particles thereby preventing agglomeration of particles, and to provide charges to the particle surface. After the surface modification, the average particle size of TiO_2 was increased from 30–50 nm to 80–100 nm. The increase in the particle size is believed to be due to the polymeric coating. The chemical structure of the neat and the modified TiO_2 was investigated by FTIR spectroscopy. As shown in Figure 2, the characteristic peak resulting from the Ti-O-Ti backbone was found between 850 and 400 cm^{-1} in both the neat and the modified TiO_2 [9]. Meanwhile, a strong peak due to the carbonyl absorption at 1730 cm^{-1} was only found in the surface modified nanoparticles. It can be confirmed that the surface of neat TiO_2 was successfully coated by acrylic copolymers. Figure 3 exhibits the electrophoretic movement of the surface modified TiO_2 particles under the electric field. A simple electrophoretic cell was fabricated to monitor the migration of electrophoretic nanoparticles. It was made of two parallel, ITO coated transparent electrodes with a 210 μm gap space, which was filled by TiO_2 particles in a low dielectric medium. While the neat TiO_2 particles migrated at $\pm$ 150 V, the surface modified TiO_2 particles started to move at $\pm$ 70 V with the same response time. The fact that the modified TiO_2 particles moved at a much lower voltage may be due to the presence of charge moieties on the surface.

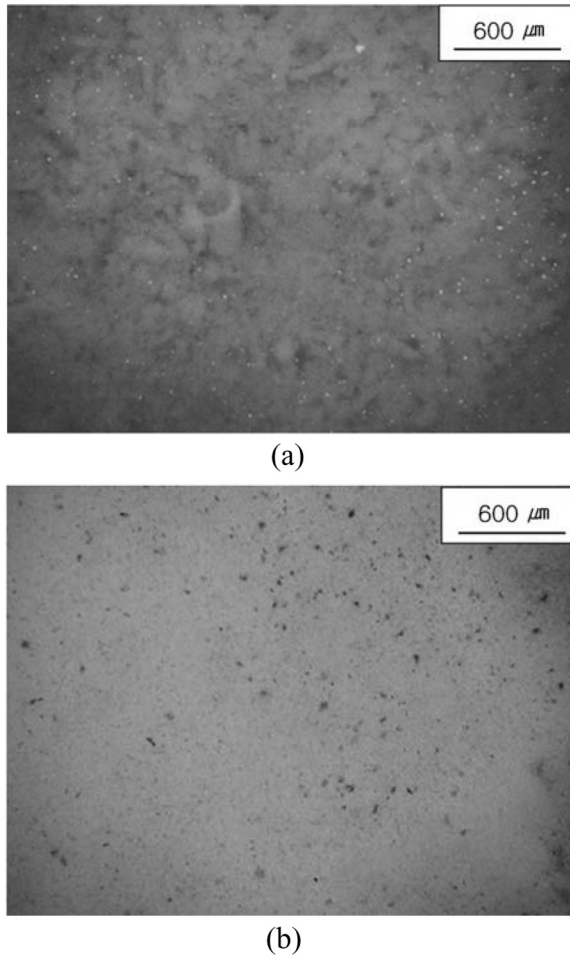
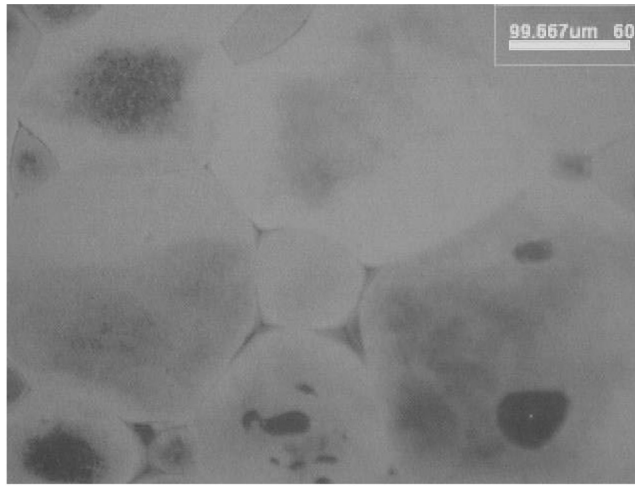
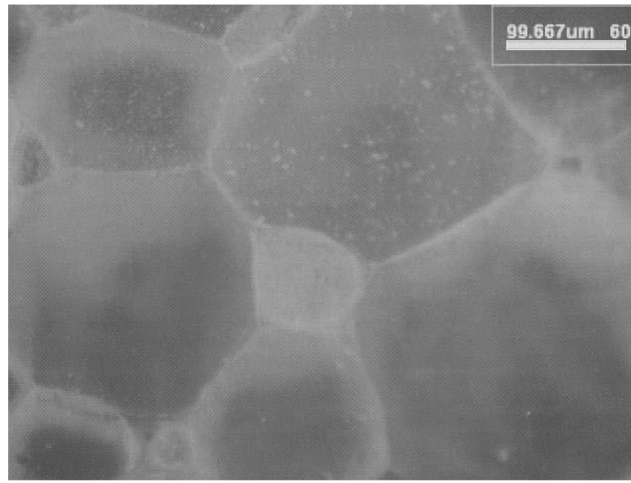


FIGURE 3 Optical micrographs showing the migration of (a) neat and (b) the surface modified TiO_2 nanoparticles in a positive electric field.

Finally, the modified nanoparticles were used as electrophoretic particles and were encapsulated by the complex coacervation of gelatin and gum Arabic. The shape of the microcapsules was spherical and their average diameter ranged from 150 to 200 μm. Moreover, their surface was smooth and any leakage of volatile oils, which were encapsulated, was not observed. Therefore, we could conclude that stable core-shell microcapsules were obtained. Figure 4 shows the electrophoretic movement of the surface modified TiO_2 particles in the microcapsules.



(a)



(b)

FIGURE 4 Optical micrographs showing the migration of the surface modified TiO_2 nanoparticles in the microcapsules when (a) positive or (b) negative electric field was applied to the electrode.

The microcapsules prepared in our study using the coacervation method had more flexible walls [10], compared with microcapsules produced by in-situ polymerization [11]. Also the layering of those microcapsules on the electrode could be done much more easily.

When the electric field was reversed from positive to negative, the cell, which contained a blue dye, clearly changed its color from white to blue because of the up and down movement of the modified TiO_2 particles in the capsule.

CONCLUSIONS

To increase both the sensitivity and the life time of the electrophoretic particles, the surface of TiO_2 particles was modified by acrylic copolymer. Core-shell type microcapsules containing electrophoretic nanoparticles were formed by the complex coacervation of gelatine and gum Arabic. When an electric field was applied to the simple electrophoretic display cell constructed with the microcapsules, a clear change of color of the cell within a short time was observed due to the migration of the modified TiO_2 in the microcapsules. The microcapsules prepared by the coacervation method were found to be superior to those made by the in-situ polymerization.

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