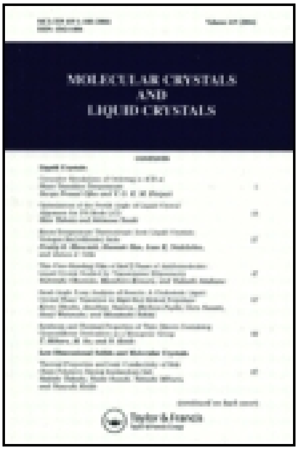

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Preparation of Electrophoretic Nanoparticles for Display Applications

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To cite this article: Tae Hee Kim & Yong Ku Kwon (2007): Preparation of Electrophoretic Nanoparticles for Display Applications, Molecular Crystals and Liquid Crystals, 464:1, 145/[727]-151/[733]

To link to this article: http://dx.doi.org/10.1080/15421400601030779

Mol. Cryst. Liq. Cryst., Vol. 464, pp. 145/[727]–151/[733], 2007
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400601030779

Preparation of Electrophoretic Nanoparticles for Display Applications

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Electrophoretic titania-coated polymer nanoparticles, hollow titania nanoparticles and colored polymeric nanospheres were prepared. The charged polymeric nanospheres were manufactured by emulsifier-free emulsion polymerization of methyl methacrylate, ethylene glycol dimethacrylate,butyl acrylate, [2-(methacryloxy) ethyl] trimethyl ammonium chloride. TiO_2 *coated polymeric nanoparticles were successfully synthesized by the use of the charged polymeric nanoparticles in various reaction media. Colored polymeric nanoparticles based on the positively-charged polymeric nanoparticles were also prepared by disperse dyeing process. The morphology and properties of the colored particles were characterized by using scanning electron microscopy (SEM), UV/visible (UV/Vis) and photoluminescence spectra (PL). The electrophoretic characteristics and mobility of these colored polymeric nanoparticles were also characterized.*

Keywords: electronic paper; emulsifier-free emulsion polymerization; nanoparticles; titania

INTRODUCTION

Recent research effort has focused on developing nanostructured materials in an attempt to expand the range of materials available for the applications in many practical uses. The preparation of nanoparticles in the submicron diameter range has been an active research area of materials research. In recent years, inorganic or organic

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Funding for this work was provided by research grant from the Korea Science and Engineering Foundation (KOSEF) through the Optics and Photonics Elite Research Academy (OPERA), an official KOSEF-created engineering research center (ERC) at Inha University, Korea.

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polymer nanoparticles are of particular interest due to their unique electrical, magnetic, catalytic, mechanical, chemical and optical properties over the single component materials [1–4]. This type of nanoparticles are usually coated with a ceramic or polymer precursor and treated to polymerize these precursors into a shell of a desired thickness, and then removed by calcination or dissolution to create the hollow center.

Nanoparticles with a low-index core and a high-index shell such as titania are very useful as catalysts and as white pigments. However, titania-coated nanoparticles are difficult to synthesize because of the reactivity of the titania precursors which makes it difficult to control their precipitation. This easily causes the core particles to aggregate or the titania to form separate particles.

In this study, we prepared the hollow nanoparticles with a polystyrene core and a titania shell. The polystyrene (PS) cores were synthesized by the emulsion polymerization technique. The surface charge of the PS cores was set to be positive by the selection of the initiator and then coated with the negatively charged titania precursor to form an organic-inorganic nanoparticles. To prepare the hollow nanoparticles, the polymer cores are calcined at high temperatures or dissolved in organic solvents. These titania particles were used as electrophoretic nanoparticles due to high refractivity, reflectivity and electrophoretic properties [5].

Here, we report a simple synthetic approach to prepare hollow titania nanospheres, titania coated polymer nanoparticles and colored electrophoretic polymer nanoparticles for the realization of electrophoretic displays based on nanoparticles. We built the monodisperse core-shell nanosphere based on the cationically-charged copolymer core. Such copolymer core, comprised of styrene, butyl acrylate and cationic [2-(methacryloxy)ethyl]trimethyl ammonium chloride (MOTAC), was prepared by soap-free emulsion polymerization. MOTAC and AIBA strongly induced the cationic charge onto the surface of the polymer core, which facilitates the rapid adsorption and uniform coating with the negatively-charged titania precursor. Colored electronic PMMA based nanoparticles were prepared by high temperature-assisted disperse dyeing.

EXPERIMENTAL

Materials

Methyl methacrylate(99%), ethyleneglycol dimethacrylate(98%), styrene(99%), butyl acrylate(99 +%), [2-(methacryloxy)ethyl] trimethyl ammonium chloride (MOTAC, 75 wt% in water), 2,2′-azobis(2-methylpropionamidine) dihydrochloride (AIBA, 97%), titanium(IV) butoxide(97%) and poly(vinylpyrrolidone) [PVP, weight average molecular weight (Mw) of 55,000] were purchased from Aldrich. Disperse red 152 was obtained by Kyung-In corporation and was used without further purification.

Emulsifier-Free Emulsion Polymerization

Cross-linked copolymer nanoparticles were prepared by emulsifier-free copolymerization of MMA, EGDMA and MOTAC using AIBA as an initiator. Polymerization was carried out in a 250 ml round flask equipped with a stirrer, reflux condenser and inlet system for nitrogen at 70°C for 20 hrs. These monomers were dispersed in water. Then, the AIBA initiator was added to a reactor with stirring with a speed at 300 rpm. After polymerization, the particles were purified by three centrifugation/redispersion cycles in distilled water. The final nanospheres were obtained by freeze drying.

Preparation of Hollow Titania Nanoparticles

The procedure to prepare the core-shell nanospheres consists of two steps: the adsorption of PVP on the cationic polymeric colloids and the adsorption of the hydrolyzed titania precursor on the PVP-adsorbed polymeric colloids, followed by the growth of titania shell. The negatively-charged titania precursors were rapidly adsorbed onto the positively charged polymer colloids by charge density matching. To remove the polymer cores, these titania-coated polymer colloids were placed in a furnace, which was heated to 500°C fot 3 hrs.

Coloring of the Polymer Particles

PMMA nanoparticles and a disperse dye were placed in water at pH ~ 4.5 and disperse dyeing was carried out at 110°C for 1 hr in a 250 ml reactor equipped with a stirrer, reflux condenser.

Characterization

The size and morphology of the nanoparticles were investigated by a Phillips CM-220 Transmission electron microscopy (TEM) and Hitachi S-4200 scanning electron microscopy (SEM) measurements. Electrophoretic mobility measurements were measured on an ELS-8000 (Otsuka Electronics) with dilute suspensions in dielectric media.

X-ray analysis was carried out in a Philips PW1847 X-ray diffractometer, operated at 40 kV and 100 mA, using reflection geometry and Cu Kα radiation (wavelength $\lambda = 0.15418\,\text{nm}$).

RESULTS AND DISCUSSION

Figure 1 shows the TEM images the cationic polystyrene spheres as a template (a), titania-coated particles (b) and hollow titania nanospheres (c). The coated spheres are also monodisperse. During the adsorption of titania precursor onto the PS cores, we also added PVP to prevent the particles from coagulating each other. The PVP adsorption and the titania-coating steps were carried out in ethanol. Poly(St-*co*-BA-*co*-MOTAC) nanospheres with an average diameter of approximately 175 nm was used as a template.

In the early stage of reaction, sol particles of the negatively-charged titania precursors were attached onto the positively-charged surfaces of poly(St-*co*-BA-*co*-MOTAC) nanospheres by electrostatic interactions. The low concentration of titanium butoxide was used to make the sol and its gelation proceeded slowly in a bulk solution. However, the adsorbed sol particles located on the surfaces of the polymer nanospheres increased their local concentration, which led to an increase of the gelation speed of the titania sols to form a titania shells on the polymer nanospheres. The final size of the coated spheres was ~230 nm, which estimated the average thickness of the titania shell as ~25 nm.

These particles can further be turned into hollow spheres both by calcination. The hollow titania shell consisted of small crystallites which were calculated to be 13.8 nm using Scherrer equation from X-ray diffraction (WAXD) patterns (Fig. 2). Based on the peak width of the most intense peak at 20~25°, which was assigned as (101) peak of anatase type titania crystal.

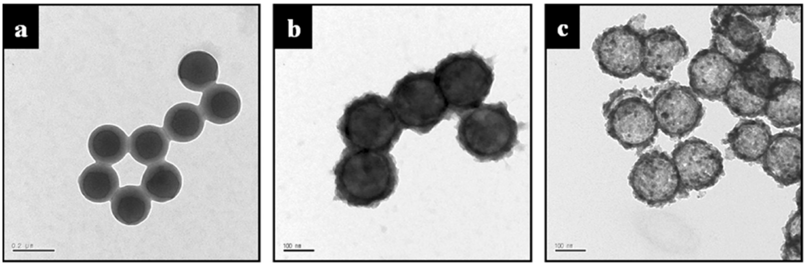

FIGURE 1 TEM images of (a) positively-charged PS nanoparticles, (b) titania coated composite nanoparticles and (c) hollow titania nanoparticles.

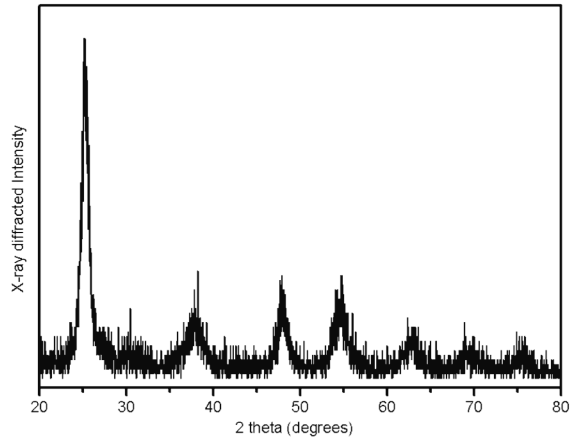

FIGURE 2 X-ray diffraction patterns of hollow titania nanospheres.

SEM images of the noncolored PMMA nanoparticles and colored PMMA nanoparticles are shown in Figure 3. PMMA nanoparticles were cross-linked by ethyleneglycol dimethacrylate (EGDMA). Disperse dyes have low solubility in water, but they can interact with the carbonyl group of PMMA chain by forming dispersed particles. The general structure of disperse dyes is small, planar and non-ionic, with attached polar functional groups like $-NO_2$ and $-CN$. The shape makes it easier for the dye to slide between the tightly-packed polymer chains, and the polar groups improve the water solubility and the dipolar bonding between dye and polymer and affect the color of the dye. The dye is generally applied at temperatures of about $110 \sim 130$°C. At this temperature, thermal agitation causes the polymer's structure to become looser, opening gaps for the dye molecules to enter. It was found that coloring of PMMA particles were

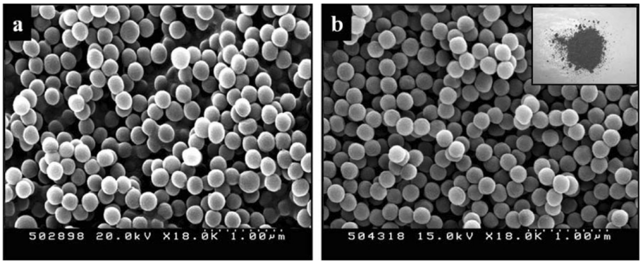

FIGURE 3 PMMA nanoparticles: (a) before dyeing and (b) after dyeing.

TABLE 1 Zeta Potential Analysis in Aqueous Media (Neutral pH) (a: Positively PS Nanoparticles, b: Titania-Coated PS Particles, c: Hollow Titania Nanoparticles and d: Red-Colored PMMA Nanoparticles)

Sample	Zeta Potential (mV)	Mobility (cm^2/Vs)	Electric field (v/cm)
a	$+47.94$	$+3.642 \times 10^{-4}$	158.94
b	-9.20	-6.984×10^{-5}	159.85
c	-21.03	-1.062×10^{-4}	160.37
d	$+43.07$	$+3.141 \times 10^{-4}$	159.11

successfully achieved by the transfer of dye into the PMMA without altering the size or morphology of the particles. The interactions between dye and polymer are thought to be Van der Waals and dipole forces.

The ζ-potential and electrophoretic mobility of the coated nanospheres was $-9.2\,mV$ and $-6.98 \times 10^{-5}\,cm^2/Vs$, respectively. The ζ-potential of the hollow titania was $-21.2\,mV$, which was negatively larger than one measured from titania-coated polymer nanospheres (Table 1). The electrophoretic mobility of the hollow titania was $-1.06 \times 10^{-4}\,cm^2/Vs$, which was also larger than one measured from the titania-coated polymer nanospheres. Due to the removal of the polymer cores, the negatively-charged particles moved more easily in an electric field. The surface charge of disperse dyed PMMA nanoparticles was measured to be positive at electric field because of using the cationic comonomer (MOTAC) and initiator (AIBA). The ζ-potential value and electrophoretic mobility were indicated $+43.07\,mV$ and $3.141 \times 10^{-4}\,cm^2/Vs$, respectively.

CONCLUSIONS

We have prepared the hollow titania nanoparticles and the electrophoretic colored polymeric nanoparticles for electronic paper applications. The nanoparticles with the organic core and the inorganic shells 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 calcination of the polystyrene core, the hollow titania nanoparticles were also prepared. Electrophoretic polymeric particles were prepared by emulsifier-free emulsion polymerization. Then, colored electronic polymer particles were manufactured by disperse dyeing. These particles were investigated by the ζ-potential analysis and we found that it moved in electric field.

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