



Size tuned electrophoretic pyrazoline nanoparticles prepared through dispersion–polymerization

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ABSTRACT

Highly monodispersed electrophoretic particles of size ranging from 550 to 160 nm could be prepared through dispersion–polymerization of methyl methacrylate and ethylene glycol dimethacrylate in presence of pyrazoline nanoparticles in a methanol–water mixture. The size of the fabricated electrophoretic particles could be controlled by adjusting the concentration of surfactant. Stearic acid, used as surfactant during the polymerization process also acts as charge controlling additive to control the electrophoretic mobility of the particles. Maximum electrophoretic mobility ($-7.513 \times 10^{-5} \text{ cm}^2/\text{V s}$) was obtained for the 400 nm electrophoretic particles prepared with 1.5 wt.% of stearic acid surfactant. The electrophoretic display cells prepared with our electrophoretic particles reveal good current voltage characteristics and color change under applied bias voltage.

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1. Introduction

Since the first report of electrophoretic image display (EPID) in 1970s [1,2], a considerable effort has been made to develop efficient materials for the fabrication of flexible low-cost EPIDs [3]. Application of EPIDs ranges from smart identity cards, electronic newspapers, electronic books, to wearable computer screens [1–6]. Fluorescent inorganic semiconductor and metal nanoparticles have been extensively used as EPID material due to their size tunable optical and electronic properties [7,8], and several display devices like transmissive liquid crystal display, organic light emitting diode display, field emission display, and plasma display have been fabricated [9,10]. However, the use of those generally brittle inorganic materials and common fussy manipulation techniques frequently make the EPIDs inefficient [7,11]. Therefore, recently the research has been focused on the application of organic molecular materials in EPIDs to replace inorganic materials. Apart from their flexible and diverse synthesis methods, organic materials are of low cost, low weight, and flexible [7,11]. While the size dependent fluorescent properties of perylene and phthalocyanine nanoparticles have been demonstrated by Nakanishi et al. [12], Fu and Yao have reported the size dependent optical properties of 1-phenyl-3-((dimethylamino)styryl)-5-((dimethylamino)phenyl)-2-pyrazoline (PDDP) nanoparticles [11]. Pyrazoline derivatives have been widely used as the optical brighteners for synthetic textiles, papers, fabrics and hole-conveying mediums in photoconductive materials owing

to their strong fluorescence [13–17]. Recently, we have reported the synthesis of size-tunable nanoparticles of 1-phenyl-3-naphthyl-5-((dimethylamino)phenyl)-2-pyrazoline (PNDP) from ten to hundreds of nanometers via reprecipitation method, and their size dependent optical properties [18,19]. In the present study, we report on the fabrication of electrophoretic nanoparticles by encapsulating pyrazoline nanoparticles in methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDMA), MMA-co-EGDMA (Fig. 1), which can be used as efficient color display material for E-papers on adding charge controlling additives.

2. Materials and methods

2.1. Materials

4-(Dimethylamino)aldehyde, sodium ethoxide, 2'-acetone, phenyl-hydrazine, methyl methacrylate (MMA), ethylene glycol dimethacrylate (EGDMA), 2,2'-azobis(2-methylpropionamide) dihydrochloride and stearic acid were purchased from Aldrich Chemical Co., and used as received. All the solvents were obtained from Junsei Chemical Co. and used without further purification. Indium–tin-oxide (ITO) coated glass slides with sheet resistance of 30 Ω/sq were obtained from Samsung Corning Co.

2.2. Preparations of pyrazoline nanoparticles

1-Phenyl-3-naphthyl-5-((dimethylamino)phenyl)-2-pyrazoline was synthesized according to our previous report [18]. The structure and composition of the material were confirmed by NMR

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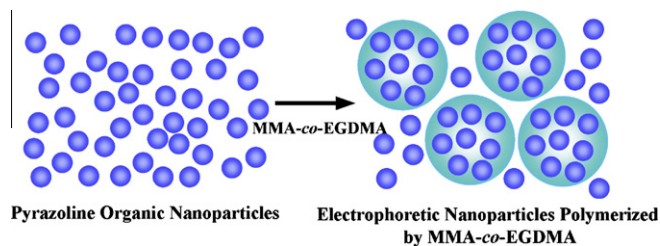


Fig. 1. Reaction scheme for the formation of electronic ink particles by the free-radical polymerization of MMA-co-EGDMA.

and mass spectroscopy (MS). The pyrazoline nanoparticles were prepared by precipitation method, where an acetone solution of pyrazoline (1.0 mM) was injected into water under vigorous stirring, and the pyrazoline molecules aggregate to form particles dispersed in water. By evaporating the water, the white powder of pyrazoline nanoparticles was obtained. The size of the nanoparticles could be controlled by changing the temperature of water and the volume of pyrazoline solution injected into it. For example, when 300 and 250 L of pyrazoline solution were injected into the water (10 mL) at 25 °C, pyrazoline nanoparticles of about 190 and 140 nm average sizes were obtained.

2.3. Synthesis of electronic ink particles by dispersion-polymerization

First, 240 mL of aqueous colloidal pyrazoline dispersion (40 nm particle size) was mixed with 60 mL of methanol under stirring in N₂ atmosphere at 60 °C. Then 0.285 mol (30.2 mL) of methyl methacrylate, 7.5 mmol (1.4 mL) of ethylene glycol, and 0.47 g of stearic acid were added into the previous solution. An aqueous solution of 2,2'-azobis(2-methylpropionamide) dihydrochloride (0.15 g in 10 mL of water) was injected to the previous solution using a glass syringe, and the polymerization was allowed to proceed for 24 h. After the completion of the polymerization process, the reaction mixture was cooled, washed several times with water, and dried in a freeze-drier. In this work, the MMA/EGDMA weight ratio in the monomer mixture was fixed at 95:5. The size of the electronic ink particles was controlled by varying the amount of the surfactant (stearic acid).

2.4. Characterization of electrophoretic particles

The size and shape of the electrophoretic particles were monitored using a field-emission scanning electron microscope (FE-SEM: JSM-6700F). The size distribution of the electrophoretic particles was also evaluated through dynamic light scattering (DLS) using a Zetaplus 1246 (Brookhaven Instruments Corporation, USA). The surface charge of the particles was determined using a zeta potential analyzer (OTSUKA Electronics, ELS-8000). The elec-

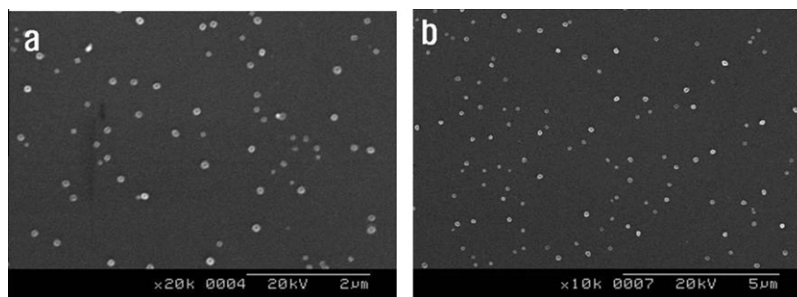


Fig. 2. Typical SEM images of pyrazoline nanoparticles of: (a) 140 nm and (b) 190 nm diameters.

Table 1
Recipe for dispersion-polymerization of MMA-co-EGDMA.

| Ingredient | | Amount |
|-------------------------|--------------|------------|
| Monomer | MMA | 28.5 g |
| | EGDMA | 1.5 g |
| Solvent | Water | 240 mL |
| | Methanol | 60 mL |
| Surfactant ^a | Stearic acid | 0.03–3.0 g |
| Initiator | AIBN | 0.15 g |

^a Surfactant concentration is varied from 0.1 to 10 wt.% of the total monomer base.

trophoretic mobility (μ) was determined by the conversion of the ζ -potential with the Smoluchowski equation, $\zeta = \mu\eta/\epsilon$, where η (=1.804 cP) and ϵ (=24.30) are the viscosity and dielectric constant of the suspending fluid, respectively [21]. The current-applied voltage characteristics of the e-paper display cell were measured with Current/Voltage Source Meter (KEITHLEY2400). Emission spectra of the nanoparticles were recorded with a Hitachi F-4500 fluorescence spectrometer.

2.5. Fabrication of electrophoretic display cells

First an ITO-coated glass slide of 30 /sq sheet resistance was cut into 3.0 × 4.0 cm² pieces. The pieces were sequentially cleaned in ultrasonic baths of isopropyl alcohol, acetone and distilled water and dried at 120 °C. Electrophoretic display cells were prepared with two ITO-coated glass plates separated by distance 100 μ m and the E-ink slurry prepared by mixing ink particles with methanol was injected to the cell through the entry port.

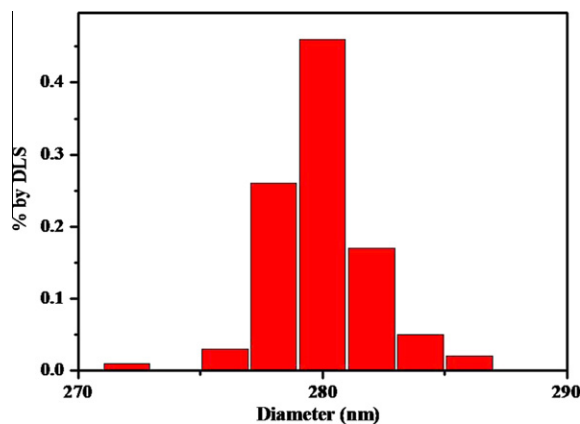


Fig. 3. Typical DLS histogram of the electronic ink particles of 280 nm average size, showing their monodispersity.

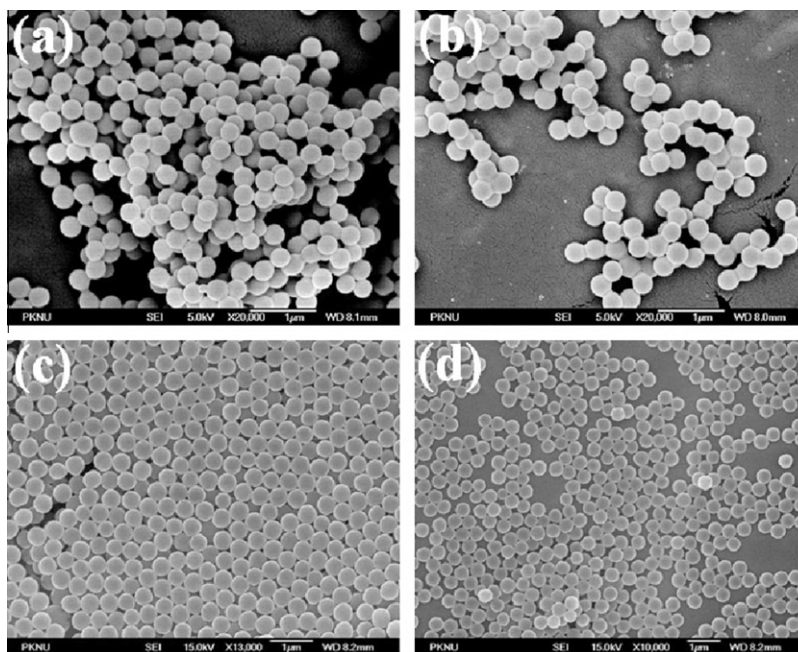


Fig. 4. Typical FE-SEM images of polymerized electronic ink particles of: (a) 300 nm, (b) 320 nm, (c) 440 nm, and (d) 470 nm average size.

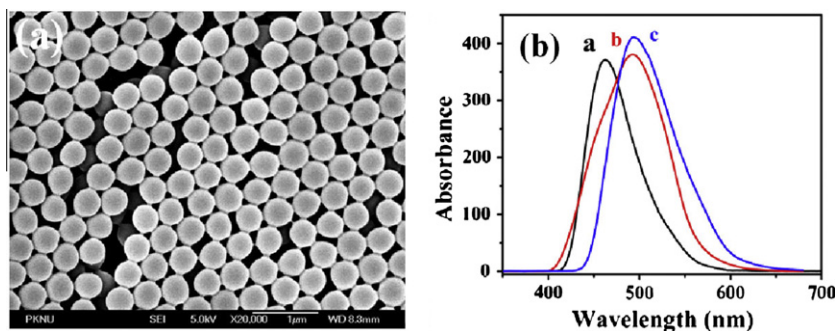


Fig. 5. (a) FE-SEM image of the electrophoretic particles of 400 nm size, and (b) fluorescence emission spectra of pyrazoline molecule in dilute acetone solution (black, 1.0×10^{-2} mM), 40 nm pyrazoline nanoparticles dispersed in water (blue), and 400 nm electrophoretic particles in methanol solution (red). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3. Results and discussion

The details of the synthesis of PNDP nanoparticles of different sizes have been discussed in Ref. [18]. In brief, 1.0 mM concentration acetone solution of PNDP was injected into deionized water at 25 °C under magnetic stirring. The size of the PNDP nanoparticles could be varied by varying the amount of injected PNDP solution in water. For example, injection of 250 μ L and 300 μ L of pyrazoline acetone solutions (1.0 mM) in 10 mL of water produced PNDP nanoparticles of 140 and 190 nm sizes, respectively (Fig. 2). Encapsulation of pyrazoline nanoparticles by MMA and EGDMA was performed in aqueous methanol medium to stabilize them and apply as electrophoretic materials in electronic papers. Pyrazoline nanoparticles dispersed in water were added to the polymerization systems containing MMA, EGDMA, stearic acid, methanol and 2,2'-azobis(2-methylpropionamide) dihydrochloride. The detailed recipe of the polymerization process is given in Table 1. Electrophoretic particles were polymerized in an 80/20 (v/v) water–methanol mixture using 0.1, 0.5, 1.5, 3, 5, 10 wt.% of stearic acid surfactant. Addition of stearic acid provides negative charge sites on the surface of those highly monodispersed pyrazoline

particles. By varying the concentration of surfactant (stearic acid), fairly monodispersed electrophoretic particles from 470 to 300 nm diameter were obtained. Uniform size distribution of the electrophoretic particles was confirmed by dynamic light scattering (DLS) in Fig. 3. Fig. 4 presents the typical FE-SEM images of the electrophoretic particles of different sizes prepared with different concentration of the surfactant. Addition of surfactant increases the nucleation sites and helps to stabilize the formed particles [20]; both of which are favorable to reduce particle size.

Fig. 5 displays the fluorescence emission spectra of pyrazoline monomer in dilute acetone solution, bare pyrazoline nanoparticles dispersed in water, and polymer encapsulated electrophoretic particles dispersed in methanol. Increase of emission intensity of the electrophoretic particles after polymer encapsulation indicates a bare dye holding during the dispersion polymerization of MMA and EGDMA. As the particle size increased, the absorption and emission peaks of the pyrazoline nanoparticles shifted to low-energy side due to aggregate formation by stacking the molecules and increased intermolecular interaction in the nanoparticles, resulting an increased delocalization of π -electrons in the aromatic rings. This size dependent emission behavior of the pyrazoline

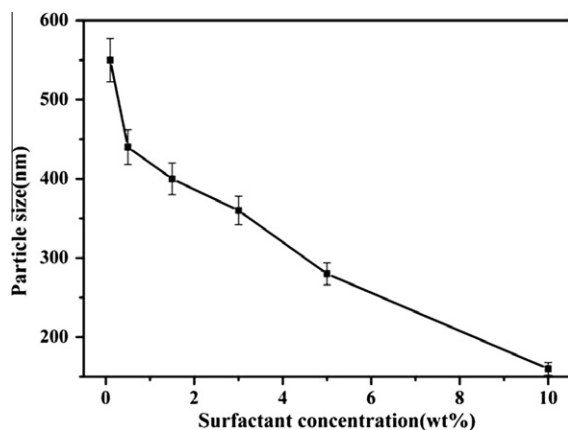


Fig. 6. Variation of particle size of the polymerized E-ink particle with the concentration of surfactant (stearic acid).

nanoparticles can be useful for the fabrication of electrophoretic particles with wide range of color display in EPIDs. It has been reported that the amount of dye in the polymerization process does not have a significant effect on either the amount of dye in the polymerized particles or on the final conversion of monomer [7]. However, we have observed that the addition of methanol to the polymerization media has a dramatic effect on the incorporation and retention of organic dye. On increasing the methanol fraction in the polymerization medium to 20%, the incorporation of dye is improved up to 97% of its theoretical value. Without methanol,

the polymer particles show about 2% of dye incorporation [20]. Apart from controlling the particle size, the used surfactant (stearic acid) acts as a charge controlling additive, proving the electrophoretic response to the particles [19]. The ink particle diameter decreased from 550 to 160 nm as the concentration of stearic acid was increased from 0 to 10 wt.% (Fig. 6) electrophoretic particles are spherical with uniform smooth surface (Fig. 5). Fig. 7a shows the effect of the surfactant concentration on the electrophoretic mobility of the particles. The electrophoretic mobility value increased initially and then decreased slightly as the negatively charged surfactant concentration increased. The maximum value of the electrophoretic mobility was $-7.513 \times 10^{-5} \text{ cm}^2/\text{V s}$ at a surfactant concentration of 1.5 wt.%. Increase of surfactant concentration increases the number of effective negative charge sites on the particle surface, enhancing their electrophoretic mobility. However, the used stearic acid is highly soluble in water. Therefore, some of the surfactant migrates from particles to the water used during their washing process. For applying in the electrophoretic test cell, electrophoretic slurry was prepared by dispersing the particles in methanol. Electrophoretic particles of three different sizes (prepared with different concentrations of stearic acid) were used for the fabrication of electrophoretic display cells. All the electrophoretic display cells containing negatively charged particles exhibited good I - V characteristics. However, the cell containing particles prepared with 1.5 wt.% stearic acid showed best I - V characteristics (Fig. 7b) due to the highest electrophoretic mobility of those particles. Fig. 8 shows the typical photographs of an electrophoretic test cell prepared by the insertion the polymerized electrophoretic particles of 400 nm size (1.5 wt.% of surfactant) between ITO glasses before and after the application of bias voltage (30.0 V). The change of displayed color and intensity on

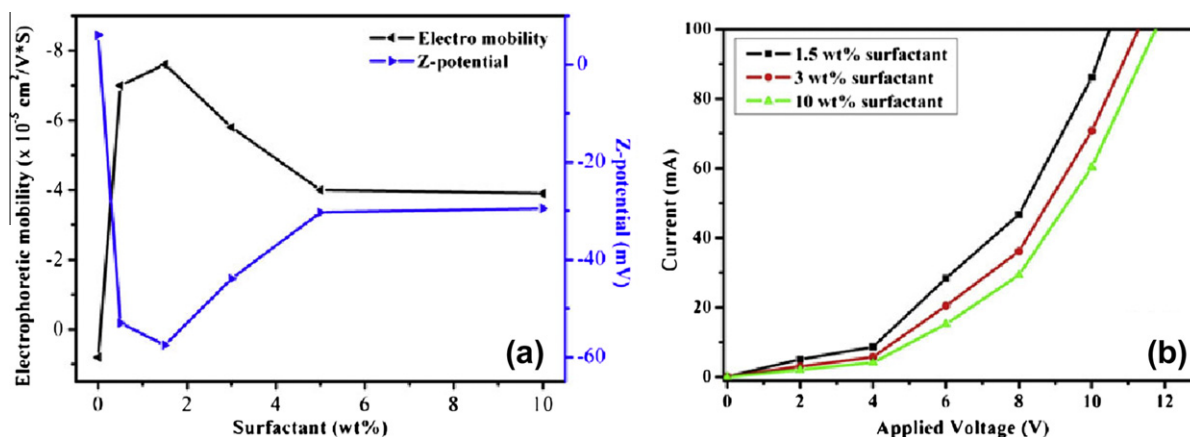


Fig. 7. Variation of electrophoretic mobility of electrophoretic particles with surfactant concentration (a), and the current–voltage curves of electrophoretic display cells prepared with ink particles of different sizes (b).

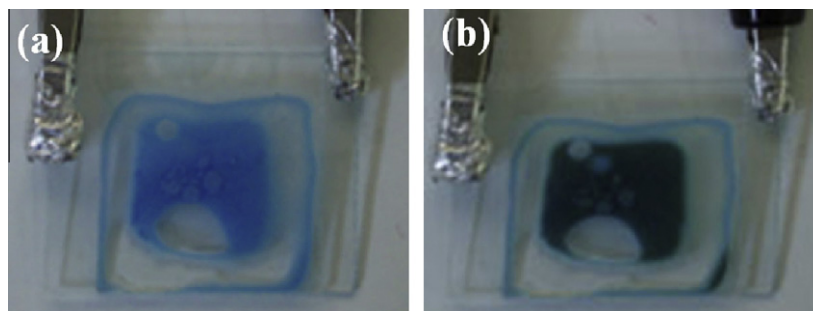


Fig. 8. The photograph of electrophoretic display cell prepared with 400 nm ink particles (1.5 wt.% of surfactant) on: (a) no applied bias, and (b) under 30 V applied bias.

the application of bias voltage is clear from the photographs. Such characteristics of the particles indicate their possible application for the fabrication of efficient color display E-paper, as has been recently reported for dye encapsulated charged organic particles [21].

4. Conclusions

In conclusion, highly monodispersed pyrazoline nanoparticles of different sizes were prepared and encapsulated in MMA and EGDMA, which on adding charge controlling additive show size dependent high electrophoretic mobility and image display behaviors. The electrophoretic particles can be applied for the fabrication of E-paper display panels. Further work on the application of these electrophoretic particles is under progress.

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