

Encapsulated-Dye All-Organic Charged Colored Ink Nanoparticles for Electrophoretic Image Display

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Since the pioneer work of Jacobson and others,^[1–7] there has been great interest in developing electrophoretic image display (EPID) technology that can be manufactured easily at low cost, with good stability, flexibility, and reliability, to replace conventional paper. Usually, inorganic materials such as TiO₂, ZnO₂, ZrO, and Al₂O₃^[8–11] have been used for the preparation of electrophoretic particles. Although various techniques for fabricating promising display devices using fluorescent inorganic semiconductor or metal nanoparticles have been widely reported, it is not easy to achieve useful EPIDs or glossy paper-like displays with these brittle inorganic materials, despite their good optical and electronic properties originating from quantum confinement effects.^[12–16] On the other hand, organic molecules can be used for preparing electrophoretic ink particles that are lighter than the inorganic ones.

Organic electrophoretic ink (E-ink) particles can be obtained through dispersion polymerization of styrene and 4-vinylpyridine (4VP) in aqueous methanol medium using poly(*N*-vinylpyrrolidone) (PVP) as a stabilizer.^[17,18] However, the selection of the polymerization method depends on the expected size and size distribution of the E-ink particles. With the dispersion polymerization method, it is easy to synthesize particles of relatively small size and narrow size distribution.^[19–22] The chargeability of the particles is a key factor in determining the speed or efficiency of the EPIDs. Thus, to control the chargeability of the particles, charge control additives providing a positive or negative charge are generally added to them.^[23–25] Enhancement of image quality requires very small particle size with a narrow size distribution of the E-ink particles for precise image control and faster response to the driving applied voltage. We have already reported the preparation and

characterization of pyrazoline-encapsulated organic nanoparticles useful as electronic paper (E-paper) materials through dispersion polymerization of styrene and 4VP.^[26]

In this Communication, we report the results of our initial investigation of the preparation and display characteristics of E-ink particles using organic molecules. These all-organic electrophoretic particles are expected to improve the mobility and reduce the cost of E-ink. The EPID cells prepared using charged organic colored ink nanoparticles display images and texts by means of charged particles that move when a voltage is applied, indicating great promise for E-books, E-newspapers, and low-power portable display applications with high brightness, good contrast ratio, and lower manufacturing cost.^[27–29]

We have used the polystyrene encapsulation method for the fabrication of stable electrophoretic nanoparticles. Addition of 4VP to the reaction mixture helped to encapsulate the nanocomposites because of its highly alkaline nature. Poly(styrene-co-4VP) particles containing organic dyes such as Acid Blue 25, Acid Red 8, and Acid Yellow 76 were prepared using ionic surfactants such as sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB) to provide electrophoretic response to the ink nanoparticles. It was assumed that the organic dye can sufficiently interact with the polymer through hydrogen bonding for the formation of nanocomposites, as shown in the schematic drawing in the Supporting Information. Due to the relatively low solubility of styrene in water, the synthesis was carried out in a methanol/water mixture (80:20 v/v) to ensure monomer solubility prior to polymerization. The electrophoretic responses of the prepared E-ink particles were examined by fabricating display cells with them. The size of the negatively charged ink nanoparticles prepared using SDS decreased with increasing surfactant concentration. As can be seen from Figures 1a–c, the surfactant provides more nucleation sites, and stability of the grown particles, which helps to control their size and shape. The ink particles are spherical with uniform smooth surface and narrow size distribution. Similar results were obtained using the cationic surfactant CTAB (Figs. 1d–f). In order to control the size of the ink particles and their surface charge density, 1.0, 3.0, and 5.0 wt% SDS and CTAB were used. The particle diameter decreased from 1.5 μm to 800 nm as the concentration of surfactant increased from 1.0 wt% to 5.0 wt%. E-ink particles of three colors with the highest electrophoretic mobility were obtained using 5.0 wt% SDS as charge control additive for different organic dyes. The scanning electron microscopy (SEM) images in Figure 2 show the formation of 800 nm particles with narrow size distribution. The polymer encapsulation process of the dyes was monitored through their Fourier transform infrared (FTIR) spectra. Figure 3a shows the

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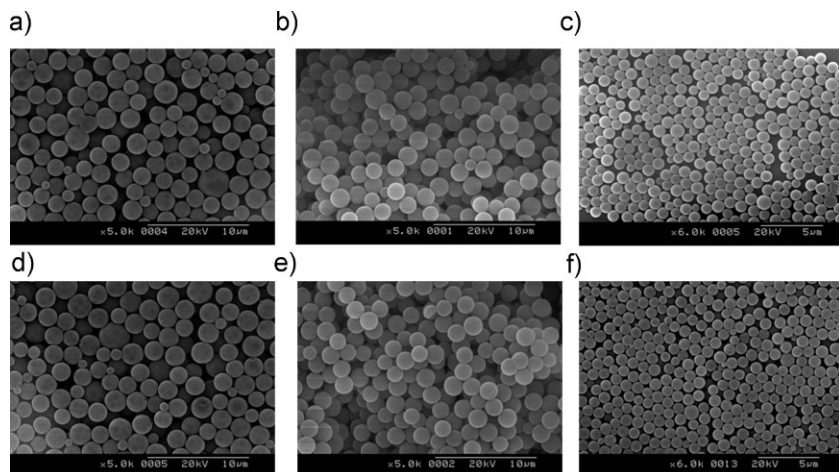


Figure 1. Typical SEM images of blue electronic ink particles with a) 1.0 wt%, b) 3.0 wt%, and c) 5.0 wt% SDS, and blue electronic ink particles prepared with d) 1.0 wt%, e) 3.0 wt%, and f) 5.0 wt% CTAB.

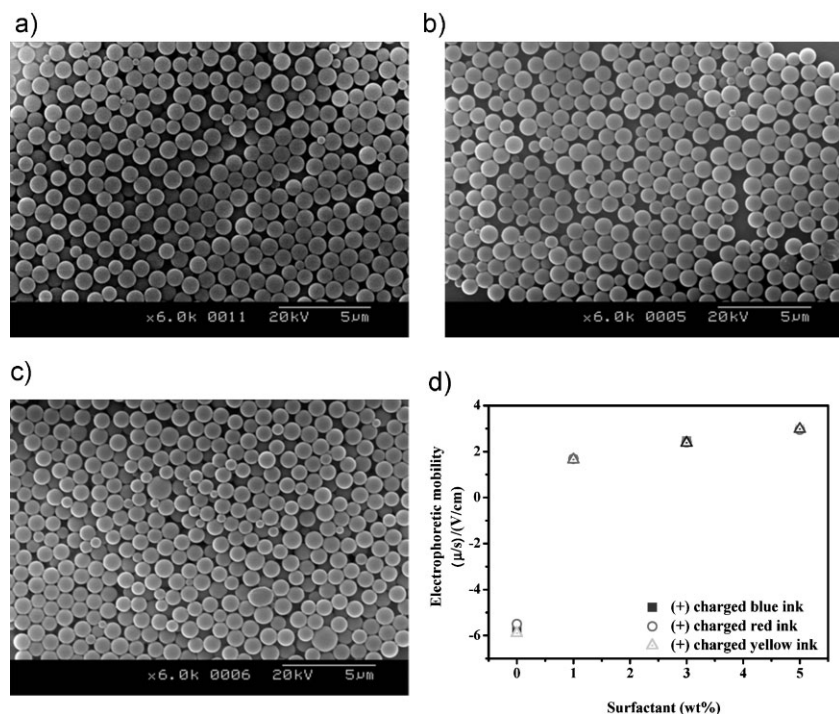


Figure 2. a–c) SEM images of negatively charged blue (a), red (b), and yellow (c) ink particles. d) Electrophoretic mobility of the positively charged ink nanoparticles of three different colors.

FTIR spectra of poly(styrene-co-4VP), poly(styrene-co-4VP) with 5 wt% SDS, negatively charged blue ink particles, negatively charged red ink particles, and negatively charged yellow ink particles. The spectrum of poly(styrene-co-4VP) revealed bands at about 1600 and 1475 cm^{-1} , corresponding to the C=C bonds of the phenyl ring of polystyrene (Fig. 3a, spectrum ii). The broad bands in the 3300–3600 cm^{-1} region of spectra ii and iii are associated with the hydroxyl group. The peaks appearing at about 1330 and 1220 cm^{-1} belong to the sulfonate (O=S=O) stretching band of SDS, and the bands in the 2800–3000 cm^{-1}

region correspond to the CH₂ and CH₃ groups of the polymer backbone (Fig. 3b). The increased intensity of the carbonyl peak at 1690 cm^{-1} in Figure 3a, spectrum iii, indicates the encapsulation of blue dye molecules by styrene and 4VP. On the other hand, the increase of the intensity of sulfonate peaks at about 1330 and 1220 cm^{-1} indicates the encapsulation of red dye molecules by polymerized styrene and 4VP (Fig. 3a, spectrum iv). The peak at about 1490 cm^{-1} belongs to the N=N stretching band of the yellow dye (Fig. 3a, spectrum v). With the addition of CTAB to electrophoretic ink particles, the intensity of the peaks between 1360 cm^{-1} and 1310 cm^{-1} increased, suggesting that the cationic surfactant CTAB was embedded with electrophoretic nanoparticles of styrene and 4VP. Characteristic FTIR peaks of the organic dye molecules are shown in Figure 3b.

The electrophoretic mobility of the ink particles was studied from the current–voltage (*I*–*V*) characteristics of test cells fabricated using them (Fig. 4). Electrophoretic test cells were fabricated by placing the encapsulated-dye ink particle slurries between two indium tin oxide (ITO)-coated glass slides with 100 μm spacing. Electrophoretic ink slurries were prepared by blending the colored ink particles (3 g) with paraffin oil (3.5 mL) and triethanolamine (7 mL). Figure 5a shows *I*–*V* characteristics of electrophoretic display cells containing ink particles. The estimated electrophoretic mobilities of the ink particles for different SDS concentrations are given in Table 1. The mobility of the particles increased with increasing surfactant concentration. On increasing the concentration of the surfactants, the number of effective charge sites over the ink particles increases, resulting in higher electrophoretic mobility. The maximum value of the electrophoretic mobility was determined to be $-2.89 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for the ink slurry prepared with 5.0 wt% SDS. Similar results were obtained using the cationic surfactant CTAB (Table 2). At surfactant concentrations higher than 5.0 wt%, the ink particles did not form well due to poor encapsulation.

The cell with blue ink particles prepared with 5.0 wt% SDS or CTAB showed the best electrical characteristics. However, all the display cells prepared with ink particles containing organic dye molecules exhibited good electrical characteristics. Figure 5b shows the *I*–*V* characteristics of the electrophoretic cells prepared with blue ink particles and the two different charge control additives. As can be seen from the *I*–*V* characteristic of the pure paraffin oil cell, paraffin is a suitable fluid for the fabrication of ink slurry. However, it becomes phase separated from the slurry quickly. Therefore, triethanolamine was added to the ink slurry as

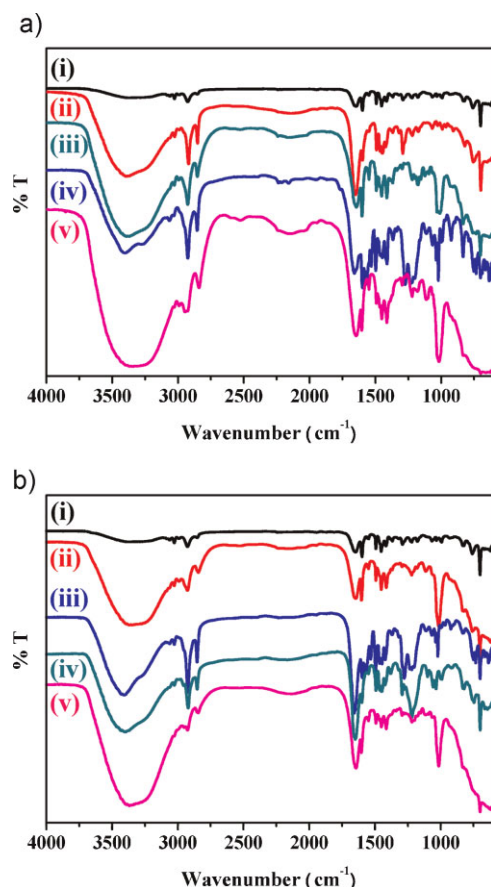


Figure 3. a) FTIR spectra of i) poly(styrene-co-4VP), ii) poly(styrene-co-4VP) with SDS, iii) negatively charged blue ink particles, iv) negatively charged red ink particles, and v) negatively charged yellow ink particles. b) FTIR spectra of i) poly(styrene-co-4VP), ii) poly(styrene-co-4VP) with CTAB, iii) positively charged yellow ink particles, iv) positively charged blue ink particles, v) positively charged red ink particles.

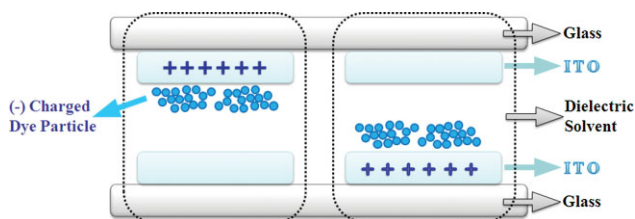


Figure 4. Schematic representation of the cross-sectional structure of an electrophoretic display cell prepared using conductive colored ink nanoparticles.

co-dispersant. From Figure 5c we see that the current is very low when no electrophoretic ink particles were added to the dispersing paraffin. The I - V characteristics of the ink particles (different colors) prepared with the same weight percentage of surfactant were similar. Figure 6 shows photographs of the display cells before and after application of a bias voltage (20.0 V). The cell in Figure 6a, which contains a mixture of negatively charged red ink nanoparticles and positively charged blue ink

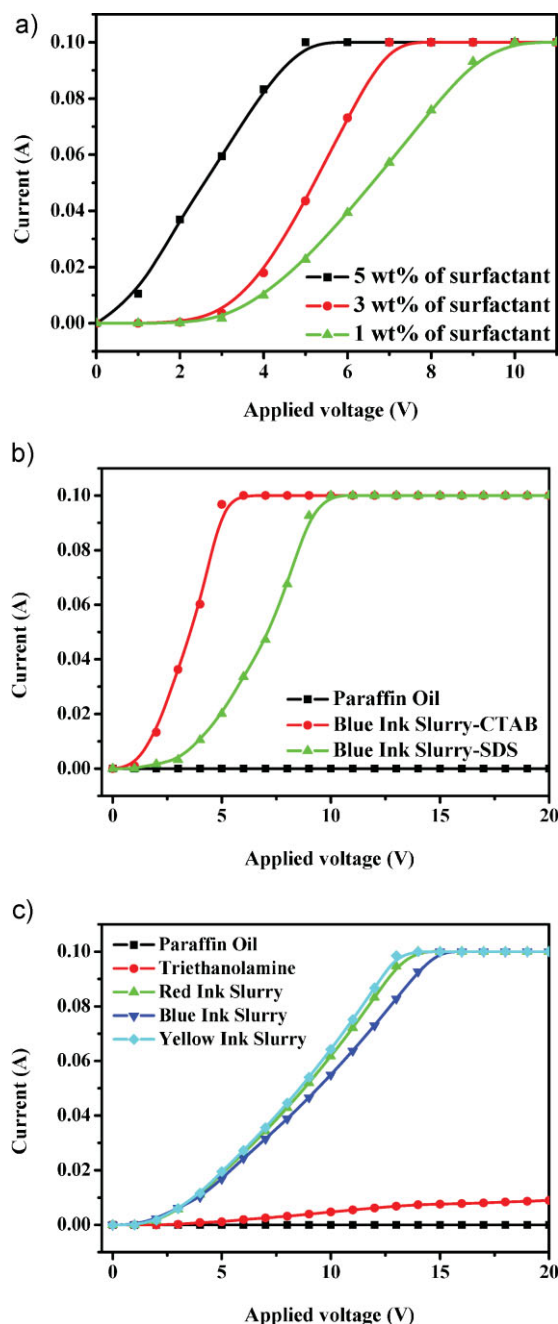


Figure 5. I - V characteristics of a) blue ink particle slurries prepared with different contents of CTAB in paraffin oil, b) paraffin oil and blue ink particle slurries prepared with 5% CTAB and 5% SDS, c) paraffin oil, triethanolamine, and blue, red, and yellow ink particle slurries prepared in paraffin/triethanolamine mixture (1:1).

nanoparticles in paraffin oil and triethanolamine mixture (1:2 v/v), is a violet color. After the application of a bias voltage (Fig. 6b), blue electronic ink particles moved towards the negative ITO glass electrode (top) and red electronic ink particles moved towards the positive ITO glass electrode (bottom). On reversing the polarity of the bias voltage, the particles were pulled back in the opposite direction. The cell in Figure 6c, which contains a mixture of negatively charged yellow ink nanoparticles and

Table 1. The zeta potential values [mV] of negatively charged ink particles.

	Blue	Red	Yellow
1.0 wt% SDS	-30.12	-30.08	-30.11
3.0 wt% SDS	-36.68	-36.55	-36.64
5.0 wt% SDS	-40.86	-40.86	-40.86

Table 2. The zeta potential values [mV] of positively charged ink particles.

	Blue	Red	Yellow
1.0 wt% CTAB	27.56	27.58	27.54
3.0 wt% CTAB	40.68	39.96	39.68
5.0 wt% CTAB	42.97	42.64	42.97

positively charged blue ink nanoparticles, appears green. The cell in Figure 6e (orange) contains a mixture of negatively charged yellow ink nanoparticles and positively charged red ink nanoparticles. The change of displayed color of the cells when a bias voltage is applied demonstrates the principle of the image formation process in EPID devices (Figs. 6d,f).

In conclusion, we have successfully prepared electrophoretic ink nanoparticles by free-radical polymerization of styrene and 4VP, encapsulating organic dyes such as Acid Blue 25, Acid Red 8, and Acid Yellow 76. Positive or negative surface charge of the ink particles could be induced using CTAB or SDS surfactant during synthesis. Both the size and the surface charge density of

the ink particles could be controlled by varying the concentration of the surfactants. The mobility of the ink particles is derived from the charge of the embedded ionic surfactant. Electrophoretic cells prepared with the charged colored ink particles can display different colors on application and change of the bias voltage. These monodisperse ink particles prepared with organic dye molecules are expected to be very useful in E-paper displays in a cost-effective way.

Experimental

Materials: Methanol (Junsei Chemical Co.), used as solvent, was used as received. Styrene monomer was purchased from Aldrich Chemical Co. and inhibitor was removed by adding 10 wt% NaOH solution. 4-VP, PVP, SDS, CTAB, 2,2'-azobis (isobutyronitrile) (AIBN), paraffin oil, and triethanolamine were also purchased from Aldrich Chemical Co. and used without further purification. Acid Blue 25, Acid Red 8, and Acid Yellow 76 used as organic dyes were purchased from Aldrich Chemical Co. and used without purification. House-distilled water was passed through a four-cartridge Barnstead Nanopure II purification system consisting of macropure pretreatment to remove trace organics, two ion exchangers and a 0.2 mm hollow-fiber final filter to remove particles. The resistivity of the deionized water used as solvent was 18.3 M Ω . ITO-coated glass slides with a sheet resistance of 30 Ω sq⁻¹ were obtained from JM International Co.

Preparation of Charged Colored Ink Nanoparticles by Encapsulation Method: Electronic ink nanoparticles were prepared using the following process. Organic dyes (0.3 g) and PVP (0.3 g) were added to a solution of methanol (48 mL) and H₂O (12 mL). Different concentrations of 1 wt% (0.06 g), 3 wt% (0.18 g), and 5 wt% (0.3 g) of each ionic surfactant (SDS, CTAB) were added to the reaction mixture. After the mixture had been stirred for 2 h, styrene (0.042 mol, 4.8 mL) and 4-VP (0.01 mol, 1.2 mL) were slowly added to the reaction medium. 2,2'-AIBN (0.15 g) was added in methanol (5 mL) and sonicated for 3 min. The initiator solution (AIBN) was injected using a glass syringe, and the reaction mixture was stirred for 9 h at 65 °C under N₂. After the (co)polymerization process, the reaction mixture was washed with water five times, isolated (by centrifuging), and dried in a freeze-dryer. In this synthesis, the styrene/4-VP weight ratio in the monomer mixture was fixed at 80:20 and methanol/water as solvent also had 80:20 ratio. As organic dyes, Acid Blue 25, Acid Red 8, and Acid Yellow 76 were used.

Characterization of Colored Electrophoretic Ink Nanoparticles: The size and shape of electronic ink particles were monitored using a scanning electron microscope (Hitachi, Japan, S-2400). The size distribution of ink particles was also evaluated by dynamic light scattering (DLS) using a Zetaplus 1246 (Brookhaven Instruments Corp., USA). The optical properties of the synthesized nanoparticles were monitored through a UV-vis spectrophotometer (Hitachi, Japan, U-2001) from their optical absorption spectra. Chemical bonding of the electronic ink nanoparticles with the polymers was studied from their FTIR spectra (PerkinElmer, USA). The surface charge and electrophoretic mobility of the ink particles were determined using a zeta potential analyzer (Otsuka Electronics, ELS-8000). The I-V characteristics of the electrophoretic display cells were measured using a Keithley 2400 current/voltage source.

Fabrication of Electrophoretic Display Cells: An ITO-coated glass slide with sheet resistance 30 Ω sq⁻¹ was cut into 4.0 cm \times 5.0 cm pieces. The pieces were sequentially cleaned in an ultrasonic bath of distilled water and methanol, followed by drying at

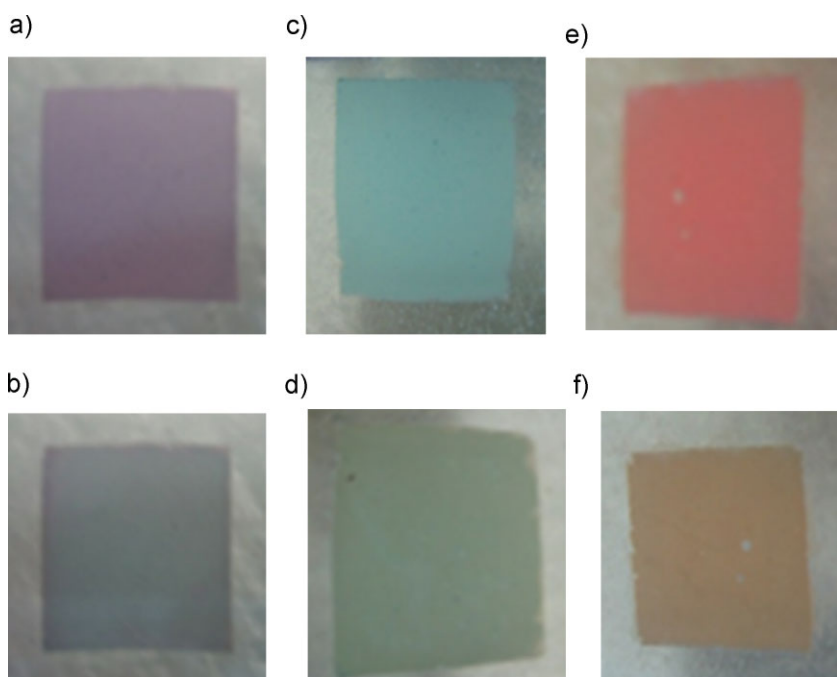


Figure 6. Electrophoretic colored ink display cells: a) blue and red ink mixed electronic ink slurry without bias, and b) after application of bias voltage; c) yellow and blue ink mixed electronic ink slurry without bias, and d) after application of bias voltage; e) yellow and red ink mixed electronic ink slurry without bias, and f) after application of bias voltage.

room temperature. Two ITO-coated glass pieces were sealed with 100 μm spacing, and electronic ink slurry, prepared by mixing charged blue, red, or yellow colored ink particles in paraffin oil and triethanolamine, was injected through the entry port to produce the electrophoretic display.

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