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## Monodisperse light color nanoparticle ink toward chromatic electrophoretic displays†

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**The facile synthesis of nanoparticles for precise image control and fast response of chromatic electrophoretic displays (EPDs) is a challenge. Herein, we report a general method to prepare pink, blue, and yellow nanoparticles with low density and a tunable size of 230–310 nm. The monodispersity is down to 0.02 and surface charges are up to 666e. Importantly, our work highlights the feasibility of chromatic nanoparticles as cost-effective candidates for electrophoretic displays.**

Since the path-breaking work of Jacobson,<sup>1</sup> electrophoretic displays (EPDs) have attracted a great deal of interest owing to low cost, paper-like high contrast appearance, ultralow power consumption, good flexibility, and reliability.<sup>2–6</sup> Li C.-L. *et al.* have synthesized SiO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub> and SiO<sub>2</sub>/Au core-shell particles with a ~3 μm diameter, achieving magneto- and electro-responsive displays by tuning the transmittance of aqueous dispersions under an external magnetic and electric field.<sup>7–9</sup> In the past few years, research has progressed so rapidly that products have been marketed, such as Amazon Kindle, and Hanwang. However, they feature 16 shades of gray and can only show white and black colors. Recently, there have been some reports on achieving chromatic EPDs (CEPDs) by combining color filters with white-black EPDs.<sup>10</sup> But the color filters decrease contrast and brightness, expending up to 70% light. A promising avenue is developed, where a pixel consists of tricolor

units, in which red, blue, and green ink particles are suspended.<sup>11–15</sup> In an electrophoretic liquid, a spherical particle with a charge  $q$  in an electric field,  $E$ , is subject to four forces when it moves from the bottom upwards: the electric force ( $F$ ), buoyancy ( $f'$ ), gravity ( $G$ ), and retarding viscous force ( $f$ ), (Fig. 1), which are given as  $F = qE$ ,  $G = 4\pi R^3 \rho_p g/3$ ,  $f' = 4\pi R^3 \rho_s g/3$ . The retarding viscous force can be described as Stokes's equation,  $f = 6\pi R\eta v$ ,<sup>16</sup> where  $\eta$  is the viscosity of the solvent,  $v$  is the particle velocity in an electrophoretic cell,  $R$  is the radius of the particle,  $\rho_p$  is the density of the particle, and  $\rho_s$  is the density of the solvent, which is smaller than 2.0 g cm<sup>-3</sup> for most solvents. The upward force must not be smaller than the downward one when the particles are driven to move up in the CEPD cell, therefore:

$$6\pi R\eta v + 4\pi R^3 \rho_p g/3 \leq qE + 4\pi R^3 \rho_s g/3 \quad (1)$$

To understand the particle movement, we hypothesize that the particles move at the largest speed in the cell and simplify eqn (1) to:

$$v = (qE + 4\pi R^3 g(\rho_s - \rho_p)/3)/6\pi R\eta \quad (2)$$

Therefore, for precise image control and fast response to the driving applied voltage for CEPDs, electrophoretic particles should be small and have high charge and low density. And the high image quality requires particles with a narrow size

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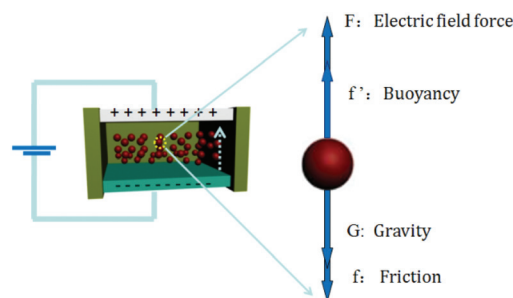
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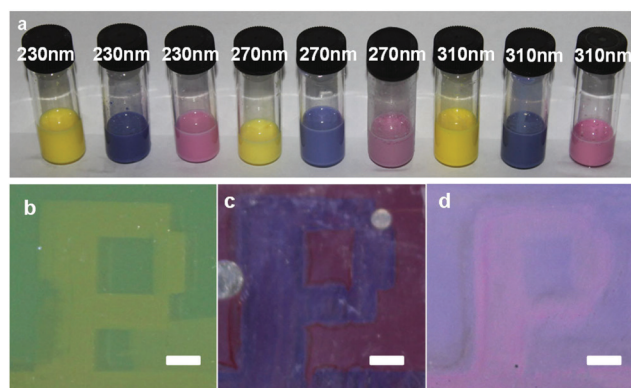


**Fig. 1** Schematic picture of the electrophoretic display and the four different forces that a spherical particle is subject to in an electrophoretic liquid.

distribution. During the past decade, several methods have been reported to prepare chromatic particles such as emulsion polymerization, and dispersion polymerization.<sup>17–24</sup> For example, Oh *et al.* reported the synthesis of encapsulated-dye all-organic charged colored ink nanoparticles between 800 and 1500 nm.<sup>25</sup> Yu *et al.* prepared acrylic-based blue electrophoretic nanoparticles with the size of 300–700 nm *via in situ* emulsifier-free emulsion polymerization.<sup>26</sup> However, the limited availability of brilliant nanoparticles with a narrow size distribution is still a challenge for developing a simple method for the large-scale preparation of various chromatic ink monodisperse nanoparticles with small size, low density and narrow size distribution.

Herein, we report a general strategy to prepare yellow, blue, pink nanoparticles with low density through combining the dye with polystyrene through emulsifier-free emulsion polymerization and to further investigate the relation of the charges of charge carriers, the radius of the particles, the conductivity, and the concentration of the electrophoretic liquid *via* experiments and theoretic calculations. Our experimental and theoretical data show a linear relation between the conductivity and concentration of the charged chromatic particles in the electrophoretic liquid. In our method, the dye molecules are hydrophobic and can be dissolved well in the styrene monomers and sufficiently coupled with polystyrene through hydrogen bonding to form chromatic nanoparticles. The average size of the chromatic nanoparticles can be controlled from 230 to 310 nm by tuning the amount of styrene from 2 to 4 mL (ESI,† Experimental section), and the monodispersity of the obtained particles is in the range of 0.02–0.08. The negative surface charges on the chromatic particles are up to 666e. It should be noted that the commercial colorful polystyrene particles with a diameter of 3–5 μm are not suitable for electrophoretic displays, because the particle size is much larger than the pixel size (1 μm), resulting in the drastic decrease of the display resolution (ESI, Fig. S1†).

Fig. 2a shows a picture of the suspensions in ethylene glycol containing 15 wt% of the chromatic monodisperse

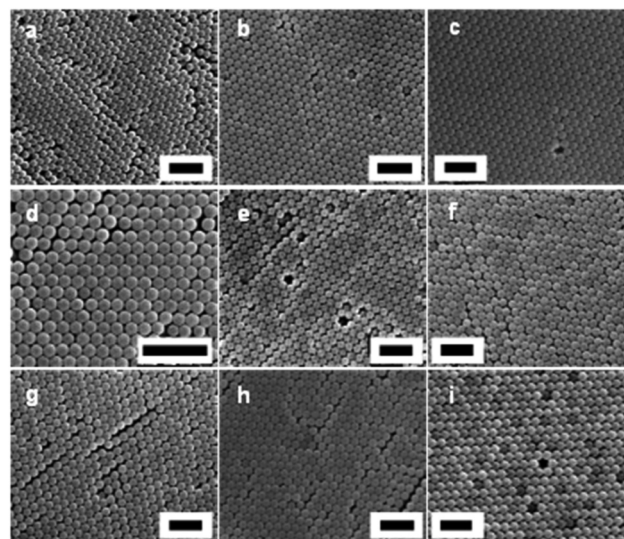


**Fig. 2** (a) Suspensions of yellow, blue and pink monodisperse nanoparticles with different sizes in ethylene glycol. (b–d) Photos of the chromatic electrophoretic displays by using 230 nm particles: (b) yellow particles, (c) blue particles, and (d) pink particles. The scale bar is 5 mm.

nanoparticles with different sizes. The observed brilliant color indicates that the particles can be used as pigments. The density of ethylene glycol is  $\sim 1.1 \text{ g cm}^{-3}$ , while that of polystyrene is  $\sim 1.05 \text{ g cm}^{-3}$ . Thus, we assume that the density of the chromatic particles and solvent is approximately equal. Eqn (2) can be rewritten as eqn (3).

$$v = qE/6\pi R\eta \quad (3)$$

The chromatic particles are used as the electrophoretic pigments to construct a CEPD cell, while the blue and red dyes dissolved in ethylene glycol are used as background colors. Under an external electric field, the chromatic nanoparticles move from the bottom upwards, thus the chromatic text is clearly displayed (Fig. 2b–d). The response time is about 6 s under a bias of 10 V. The distance between two electrodes is  $\sim 500 \mu\text{m}$  in our electrophoretic display prototype. Therefore, the obtained chromatic nanoparticles are promising blocks for a CEPD with fast response and a good contrast ratio. The bubbles in Fig. 2c are formed because of the air in the cell upon sealing. Fig. 3 shows the SEM images of the yellow, blue and pink nanoparticles with different sizes. From top to bottom, they are yellow (Fig. 3a–c), blue (Fig. 3d–f) and pink (Fig. 3g–i) nanoparticles. From left to right, the size is 230 nm (Fig. 3a, d & g), 270 nm (Fig. 3b, e & h) and 310 nm (Fig. 3c, f & i). The SEM samples were prepared by drop-casting a chromatic particle suspension on the Si wafer and drying in air. The hexagonal arrays of the chromatic nanoparticles are quite easy to be formed, indicating excellent monodispersity. For the 230, 270 and 310 nm yellow nanoparticles, the polydispersity values are 0.04, 0.02, and 0.03, respectively. For the 230, 270 and 310 nm blue and pink nanoparticles, the polydispersity values are 0.07, 0.08 and 0.06, and 0.06, 0.06 and 0.08, respect-



**Fig. 3** SEM images of the chromatic nanoparticles with different sizes: yellow nanoparticles (a: 230 nm, b: 270 nm, c: 310 nm), blue nanoparticles (d: 230 nm, e: 270 nm, f: 310 nm), and pink nanoparticles (g: 230 nm, h: 270 nm, i: 310 nm). The scale bar is 1 μm.

ively (ESI, Fig. S2†). All chromatic particles have a polydispersity value smaller than 0.1, indicating excellent monodispersity. Therefore, the obtained yellow, blue and pink nanoparticles can be used as pigments to achieve good image quality, and precise image control in CEPDs.

Fig. 4 shows the reflection spectra of the yellow, blue and pink chromatic nanoparticle (15% wt) ethylene glycol suspensions. All chromatic nanoparticles show high reflection with a steep edge, which is in good agreement with the brilliant color (Fig. 2). The yellow particles show high reflection in the range from 530 to 800 nm. For the 230 and 270 nm particles, the reflection are between 40 and 50%. For the 310 nm particles, the reflection is larger than 50%. It is because more dye molecules are coupled with polystyrene with increasing size of chromatic par-

ticles. Fig. 4b shows the reflection spectra of the blue particles, which is consistent with Fig. 2b, e & h. A peak at 450 nm is detected for all blue particles and the reflection is 29, 44, and 29% for the 230, 270 and 310 nm particles, respectively. In the range between 700 and 800 nm, the reflection of the 230 and 310 nm particles is up to 49%. And for the 270 nm particles, the reflection decreases with increasing wavelength, but the decrease of reflection is much smaller than that of the 230 and 310 nm particles. Therefore, the color of the 230 and 310 nm particles is deeper than the color of the 270 nm ones. But the reason inducing the reflection difference is still not clear and further investigation is needed. The reflection spectra of the pink particles are shown in Fig. 4c, which is consistent with Fig. 2c, f & i. In the range between 600 and 800 nm, they all show high reflection, 41–45, 45–50, and 50–59% for the 230, 270 and 310 nm particles, respectively. The reflection also increases with increasing particle size. And they all show high reflection before 450 nm, but the reflection of the 270 nm particles is larger than that of the other particles. Therefore, all particles are pink and the 270 nm particles are a little violet, as shown in Fig. 2.

The conductivity was investigated (Fig. 5). For all of the chromatic nanoparticles, the conductivity follows a linear relation as a function of chromatic nanoparticle concentration, *i.e.*, the conductivity increases with increasing concentration. Fig. 5 shows the fitting curves with the formula  $y = a + bx$ , where  $y$  is the conductivity,  $x$  is the concentration, and  $a$  and  $b$  are constant. In the suspension, the chromatic nanoparticles migrate under the influence of an external electric field, the current density,  $J(r, t)$ , can be written as eqn (4):

$$J(r, t) = \sigma E = qv(r, t)n(r, t) \quad (4)$$

where  $v(r, t)$  is the velocity of the charge carrier at the location  $r$  and time  $t$ ,  $n(r, t)$  is the number of charge carriers per unit volume,  $q$  is the surface charges of one charge carrier,  $\sigma$  is the conductivity, and  $E$  is the electric field intensity. The concentration of chromatic nanoparticles in the electrophoretic liquid,  $C$ , can be given as:

$$C = 4\pi R^3 g \rho_p n(r, t) / 3 \quad (5)$$

where  $\rho_p$  is the density of the chromatic nanoparticles,  $1.05 \times 10^6 \text{ g m}^{-3}$ .<sup>27</sup> Therefore, by combining eqn (3)–(5), we can obtain eqn (6).

$$q^2 = 6\pi R \eta \sigma / n(r, t) = 1.6498 \times 10^3 R^4 \sigma / C \\ = 1.6498 \times 10^3 R^4 K \quad (6)$$

where  $\eta$  is the kinematic viscosity of ethylene glycol,  $1.99 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ .  $K = \sigma / C$  ( $C > 0$ ). Eqn (6) indicates that the conductivity increases linearly as the concentration of the chromatic particles increases, which is in good agreement with the experimental data.  $K$  was obtained from Fig. 5 and  $q$  was further calculated using eqn (6). For the 230, 270 and 310 nm yellow nanoparticles, the values are 256, 376, and 599 $e$  respectively. For the 230, 270 and 310 nm blue nanoparticles, they are 322, 504, and 666 $e$ , respectively. And for the 230, 270 and 310 nm pink nanoparticles, they are 270, 369, and 407 $e$ ,

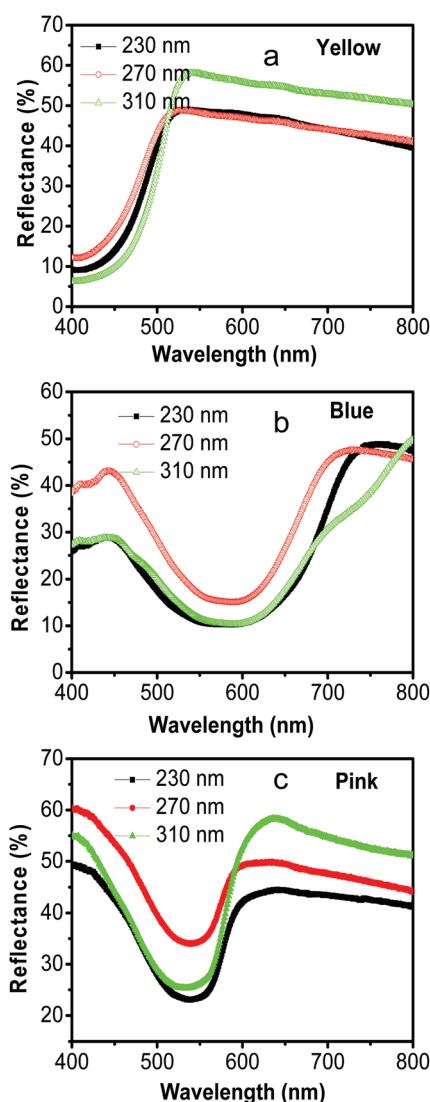
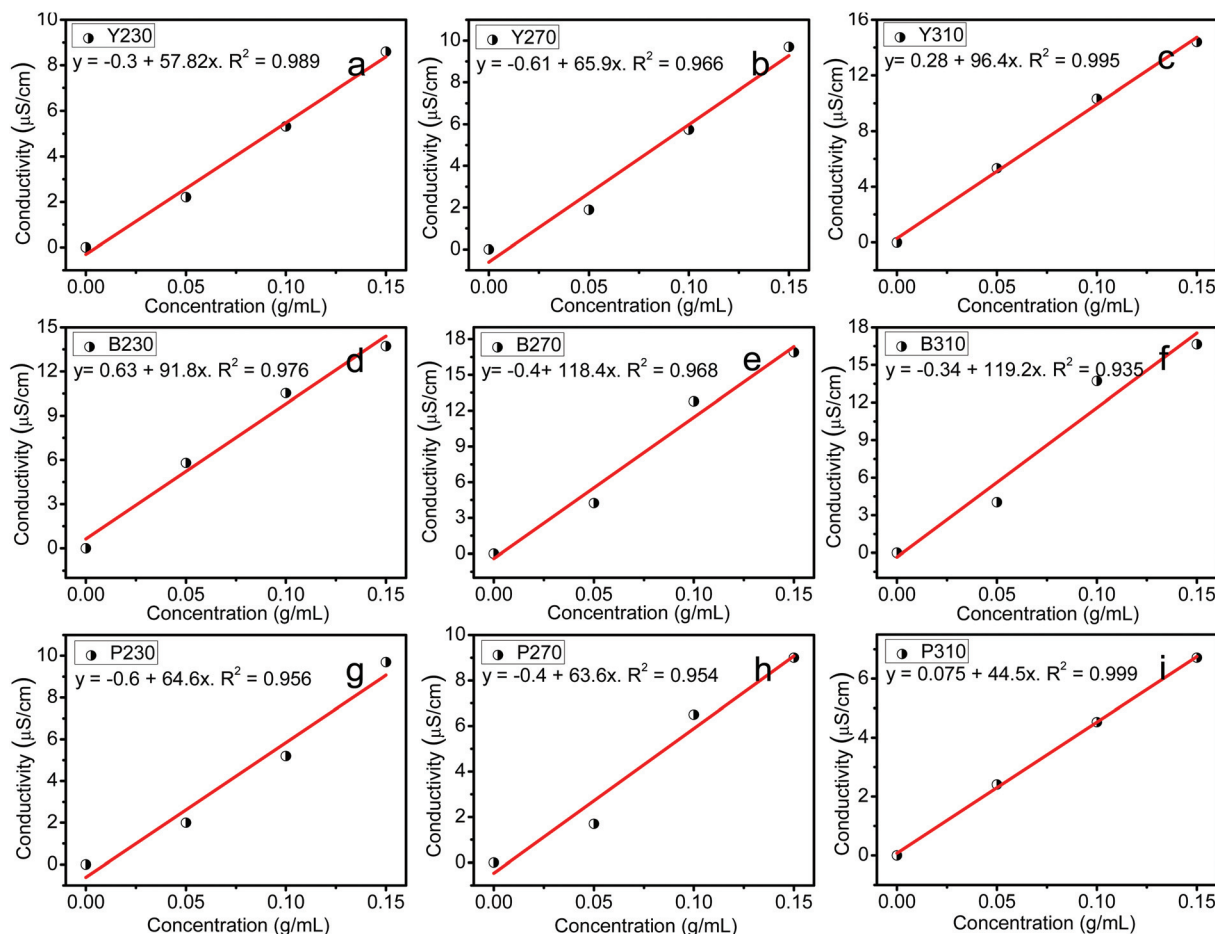


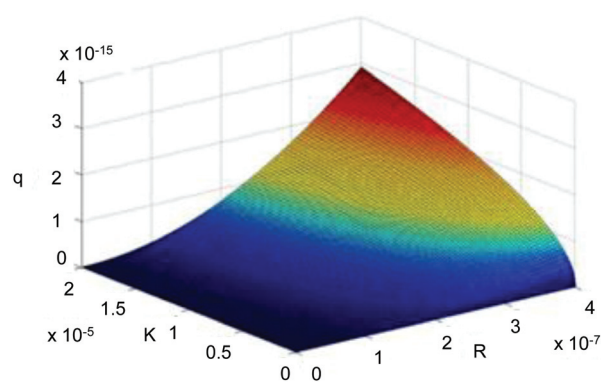
Fig. 4 The reflection spectra of the yellow, blue and pink chromatic nanoparticles in ethylene glycol: (a) yellow nanoparticles with a size of 230 nm, 270 nm, and 310 nm, (b) blue nanoparticles with a size of 230 nm, 270 nm, and 310 nm, and (c) pink nanoparticles with a size of 230 nm, 270 nm, and 310 nm.



**Fig. 5** The conductivity ( $\mu\text{S cm}^{-1}$ ) of the yellow, blue and pink chromatic nanoparticles versus the concentration in ethylene glycol: yellow nanoparticles of (a) 230, (b) 270, and (c) 310 nm; blue nanoparticles of (d) 230, (e) 270, and (f) 310 nm; and pink nanoparticles of (g) 230, (h) 270, and (i) 310 nm.

respectively. It is found that the surface charges increase as the nanoparticle size increases. It is because the surface area ( $4\pi R^2$ ) of the nanoparticle increases, and the negative  $-\text{OSO}_3^-$  species at the end of the polystyrene chain increases. The Zeta potential of the prepared chromatic PS particles is between  $-28$  and  $-50$  mV (ESI, Fig. S3<sup>†</sup>), indicating highly negative charges on the surfaces. The Zeta potential also increases with increasing particle size, which is consistent with the trend of the calculated surface charges. From eqn (3), it is found that the electrophoretic velocity of the chromatic particles shows a linear dependence on the ratio of  $q$  to  $R$ . For the 230, 270 and 310 nm yellow nanoparticles, the ratios of  $q$  to  $R$  are  $2.1 \times 10^9$ ,  $2.6 \times 10^9$ , and  $4.0 \times 10^9$   $\text{e m}^{-1}$ , respectively. For the 230, 270 and 310 nm blue nanoparticles, the ratios of  $q$  to  $R$  are  $2.8 \times 10^9$ ,  $3.3 \times 10^9$ , and  $4.3 \times 10^9$   $\text{e m}^{-1}$ , respectively. And for the 230, 270 and 310 nm pink nanoparticles, the ratios of  $q$  to  $R$  are  $2.3 \times 10^9$ ,  $2.7 \times 10^9$ , and  $2.6 \times 10^9$   $\text{e m}^{-1}$ , respectively. For the yellow and blue chromatic particles, the ratio of  $q$  to  $R$  exponentially increases as the particle size increases, and it is a linear relation for the pink nanoparticles. According to eqn (6), we demonstrate the relation between the surface charges,

the radius of the particles, and the ratio of the conductivity of the electrophoretic liquid to the concentration of chromatic particles, as shown in Fig. 6. The electrophoretic properties of the different chromatic particles can be evaluated visually



**Fig. 6** The relation between the charges of one charge carrier, the radius of the particles, the conductivity, and the concentration of electrophoretic liquid.

from Fig. 6. The bigger  $K$  and  $q$  are, the larger the chromatic particle velocity is. The  $q$  and  $K$  values are the key factors determining the electrophoretic properties of the chromatic particles and the performance of a chromatic display.

## Conclusions

A general emulsifier-free polymerization method to synthesize yellow, blue and pink chromatic particles was reported. These chromatic particles demonstrated brilliant color and high reflection up to 59%. The monodispersity was down to 0.02. A linear dependence of the conductivity on the concentration of the particles in an electrophoretic liquid was observed and hundreds of negative charges up to 666e were on the surface of the chromatic particles. Our work suggests that the chromatic nanoparticles can have good applications as electrophoretic pigments in chromatic electrophoretic displays.

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