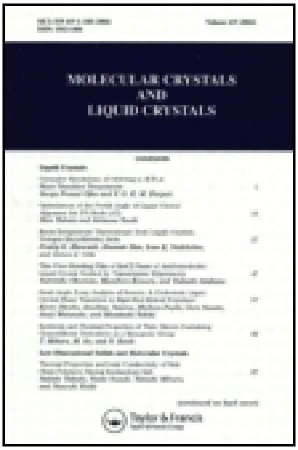

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Fabrication and Properties of Electrophoretic Display Thin Film for Electronic Paper

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The electrophoretic display thin film (EPDTF) was fabricated using gelatin/gum arabic microcapsules as display materials. The influential factors of preparing the film, which included transmittance, surface tension, viscosity, the preservative rate, and the surface morphology, were investigated. After being sandwiched with the electrodes, the reflective properties of the EPDTF were characterized by fiber-optic spectrometer. Moreover, the display property was also investigated. The results revealed that the EPDTF can be prepared with flatten surface morphology, good flexibility, fine reflective properties, and high intrinsic bistability at the binder concentration of 1.0 wt%. Furthermore, a static image can be displayed clearly by applying a voltage pulse.

Keywords: electrophoretic display; microcapsule; optical properties; thin film

INTRODUCTION

The electrophoretic ink, a novel display material which can be called encapsulated electrophoretic display, is fabricated from a two-dimensional arrangement of microcapsule containing electrophoretic composition of a dielectric fluid and particles that visually contrast with the dielectric liquid and also exhibit surface charges. As this kind of display has attributes of good brightness and contrast, wide viewing angles, state bistability, and low power consumption when compared with liquid crystal displays [1–5], it has been subjected to intense research and development for a number of years [6–15].

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To fabricate the electrophoretic display, a two step procedures often are needed after the microcapsules were prepared. That is, the prepared microcapsules were separated from the water phase by a drying process, such as spray drying, centrifugal drying, and freeze drying, etc. But in these processes, the secondary aggregation phenomenon between the capsules usually existed, which makes it hard to be redispersed when the dried microcapsules were used to fabricate the electronic ink display. In the secondary process, the dried microcapsules are mixed with a binder and printed or coated on the counter electrode to construct electrophoretic display thin film (EPDTF). Then they were sandwiched with the pixel electrode to fabricate the microencapsulated electrophoretic display. Unfortunately, in this process, the reaggregated capsules were easy to be fractured by extrusion and/or impact, which often caused the leakage of the core materials and, ultimately, had a negative impact on the display properties.

Albert et al. pointed out that this question can be solved by directly mixing the capsules with a kind of aqueous binder to form a display [16]. However, in this method, the effect of the binder on the surface morphology and the optical properties of the film were not referred. Moreover, the formation mechanism of the film was also not clear.

In this article, the gelatin/gum arabic microcapsules prepared by complex coacervation were directly used to fabricate the display film without isolation and drying. The effect of the binder on the surface morphology and the optical properties were also involved. Moreover, a preliminary mechanical model for the formation of film was proposed. By this method, the film was of good surface morphology, high flexibility, and reflective properties.

EXPERIMENTAL

Fabrication of Film

The gelatin/gum arabic microcapsules were prepared by complex coacervation [17]. After the capsules were fabricated, they were washed with deionized water for three times and filtered for primary isolation with water, which then were added in an aqueous solution of gelatin with a volume ratio of $\sim$1:1 and stirred adequately. After that, the mixture was transferred to Indium-tin oxide (ITO) coated glass and coated with a tape casting method. Thereafter, the film was dried with a low temperature.

ITO glass with a sheet resistance of $17\,\Omega/\square$ was cut into a $6.0\,\text{cm} \times 15.0\,\text{cm}$ and used as counter electrode. Another ITO glass was patterned with school badge of Northwest Polytecnical University by shadow etching technique and used as pixel electrode. The two parallel electrodes were sealed with clips after the EPDTF was fabricated.

MEASUREMENT AND CHARACTERIZATION

The optical photographs of microcapsules were observed under an optical microscope (Alphaphot-2, YS2-H Nikon, Japan), with CCD (Fijitsu, Japan) and collected photographs dealt with grey scale through a seizing card of video capture. Moreover, the surface morphologies and smoothness of the film were observed by scanning electron microscopy (SEM, JEOL JSM-6700 F) at 5 kV of an acceleration voltage. The surface morphology of the film is observed at an angle of 5°, and the sample was gold-coated to minimize the charging effect. The reflectance spectra were collected on an Ocean OpticsC-2000 fiber-optic spectrometer. Spectra were collected between the wavelengths of 350–800 nm. The response behavior of the EPDTF was also investigated by a pair of parallel electrodes.

RESULTS AND DISCUSSION

Effect of Gelatin

In this article, the main purpose is to investigate the configuration and the properties of EPDTF. As the result, the aqueous solutions of gelatin with different concentration are chosen, and the influences of binder concentration on the transmittance, surface tension, viscosity, preservative rate, and film properties are discussed in present study. It appears that these parameters have an important influence on the surface morphology of the film as described below.

Transmittance

After gelatin is dissolved in deionized water, the solution is clear and transparent but with a flaxen color. As a result, haze/scattering is not able to exist in this system. Herein, the transmittance of different concentration of binder solution is shown in Fig. 1. As is shown, the transmittance of the gelatin at 0.5 wt% is high, which almost surpasses 95% at the visible band. With the increase of the concentration, the transmittance decreases. When the concentration reaches to 1.0–2.0 wt%, there is no obvious difference in transmittance. At the concentration of 2.5%, there is a distinct decrease in transmittance, which is almost below 90%. From above, we can see that the higher concentration will have a negative influence on the optical character of the EPDTF.

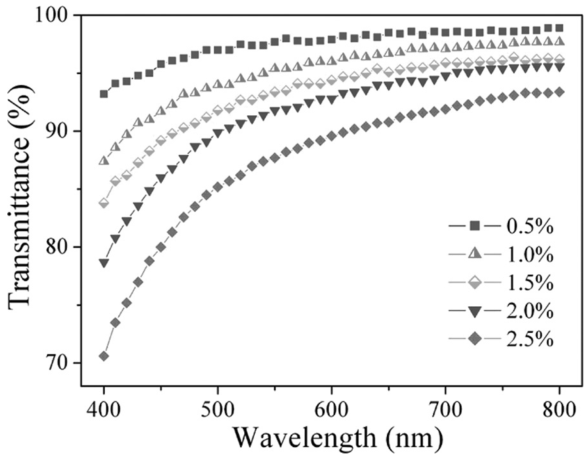


FIGURE 1 Relationship between binder concentration and transmittance.

Surface Tension and Viscosity

Figure 2 shows the surface tension and viscosity of aqueous solution of gelatin as a function of gelatin concentration. As can be seen, there is a maximum in the surface tension at 1.0 wt%, which indicates that the tension may be big enough to pack the microcapsules together and cause the deformation of the display thin film during the drying process. After that the surface tension decreases rapidly.

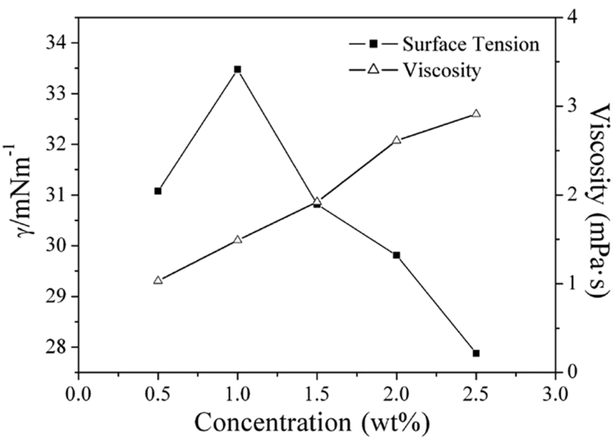


FIGURE 2 Surface tension and viscosity of binder solution as a function of binder concentration.

Moreover, from Fig. 2, it can also be seen that the viscosity keeps increasing at all concentration. It is worth to be point out that the dramatically increased viscosity is not suitable for preparing the display film. This can be explained as follows: the higher viscosity decreases the fluidity of the binder solution, which causes the capsules hard to be dispersed. Furthermore, the capsules are not able to shrink inward and packed closely during the drying process. As the result, the surface of the prepared film will be rough.

Preservative Rate

After the film is fabricated, it will be sandwiched with two parallel electrodes to realize display. For this kind of device, it is expected that the capsules within the film should be kept for a certain long period. From Fig. 3, it can be seen that the preservation rate of the film prepared with the binder concentration of 0.5 wt% is ~10% after 30 days, which is mainly owing to the rupture of the capsules. This causes the film disable to display at this state. But the films prepared with other concentration are not found the remarkable occurrence of cracking of capsules.

Morphological Study

The surface morphology using different concentration of binder is shown in Fig. 4. At the concentration of 1.0 wt%, the surface is flat

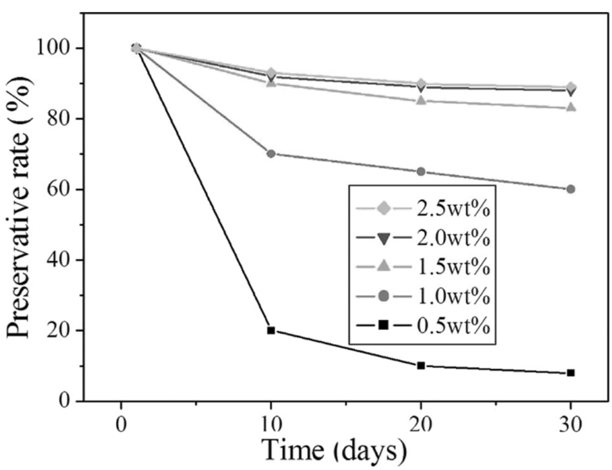


FIGURE 3 Preservative rate of the film with different binder concentration.

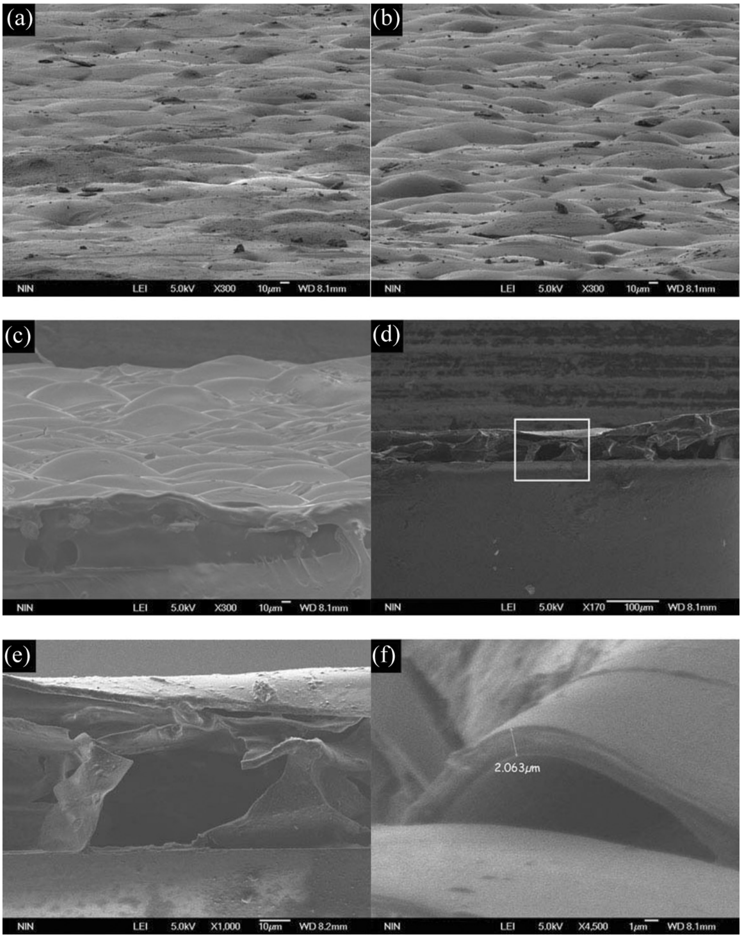


FIGURE 4 SEM images: (a), (b), and (c) surface morphology of the film with the binder concentration of 1.0%, 1.5%, and 2.0%, respectively; (d) cross-section of (a); (e) magnified view of (d); (f) thickness view of film of (a).

and smooth (see Fig. 4a). This indicates that the reflective properties of this kind of display may be enhanced by this method. Moreover, the effective contact area between microcapsules and ITO glass also can be improved by flattening the display side of the capsules. When the concentration increases to 1.5 wt%, a rough surface of the film can be observed in Fig. 4b. Whereas at the concentration of 2.0 wt%, the surface even becomes rougher (see Fig. 4c). From the cross-section of Fig. 4d, we can see that the film formed by microcapsules is made of

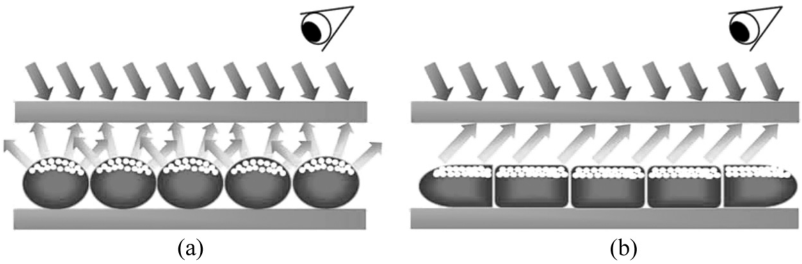


FIGURE 5 Schematic illustration of EPDTF display with different surface.

cavities with a thickness $\sim$50 μm, which is confirmed by a magnified view of Fig. 4e; and the thickness of the film wall is also observed as shown in Fig. 4f, which shows that the thickness of the film wall is $\sim$2 μm.

It is obvious that the film with regular and smooth surface morphology may endow the materials with good optical properties when they are used to display. Figure 5 illustrates the optical behavior of EPDTF with different surface morphologies. As shown, the rough surface will cause the increase of the diffuse reflecting of this kind of display, which consequently will decrease the contrast and luminance; and the saturation can also be reduced (see Fig. 5a), whereas the flatten shape will reduce intergap between the film and electrode, and the film also is able to form a quasi mirror plate. By this, the film with good optical properties can be obtained (see Fig. 5b).

SELF-ASSEMBLING PROCESS AND MECHANISM

Denkov et al. have directly observed the dynamics of 2D array formation of latex particles on solid substrate by mean of optical microscopy. They found that the formation of the array on the water–air interface is a self-assembling process [18]. Figure 6a is the image of the capsules lay for 1 min, from which we can see that most of the capsules are maintained for intact except that several capsules are deformed, and each of the capsules keeps apart. Beside this, it also can be seen that the modified TiO_2 particles in the capsules are aggregated together. After laying for 5 min, as the wall of the capsules is flexible, they are capable of deformation without leakage of core materials (see Fig. 6b). With time, the capsules are totally deformed, and the interstice between microcapsules decreases, and the capsules even cohere together after 15 min (see Fig. 6c). When the mixture is laid for 30 min, the capsules cohere together, and the particles are

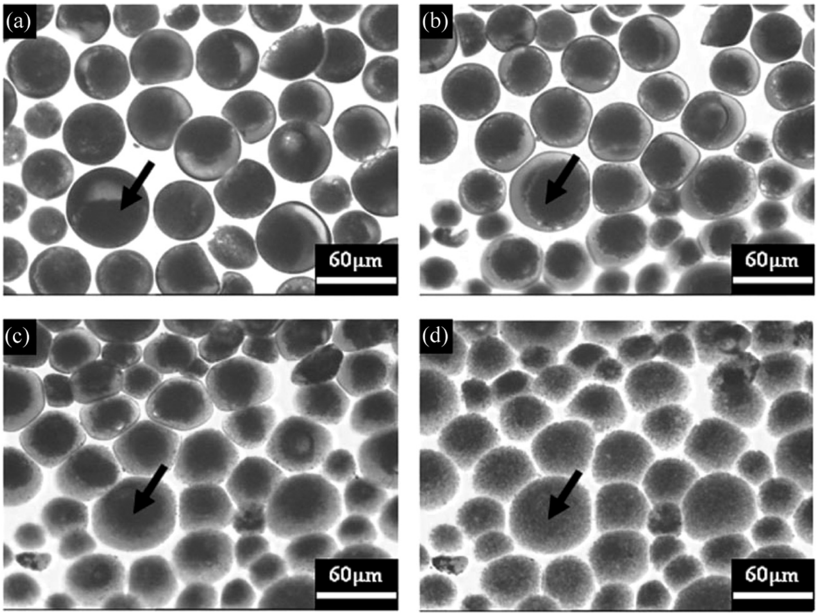


FIGURE 6 Optical images of microcapsules during self-assembling process: (a) after 1 min, (b) after 5 min, (c) after 15 min, (d) after 30 min.

distributed in capsules (as shown by arrows in Fig. 6d). After this, the EPDTF can be obtained with further absolutely drying.

On the basis of the observation above, we propose a model about the formation of the EPDTF, as shown schematically in Fig. 7. At

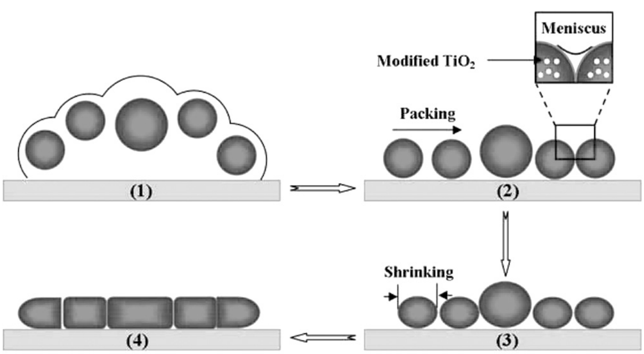


FIGURE 7 Schematic illustration of EPDTF formation mechanism: (1) microcapsules suspension supports on ITO glass; (2) microcapsules pack together; (3) microcapsules deform and shrink; (4) EPDTF is formed by further drying.

the first step, the microcapsules suspend in the aqueous solution of gelatin after supported on the ITO glass. Owing to the evaporation of water, the microcapsules suspension layer gradually thins. When its thickness of the suspension layer becomes equal to the bigger microcapsule diameter, the bigger one forms a nucleus and is encircled by the smaller neighboring microcapsules in thicker layer. The evaporation also causes the occurrence of the meniscus between the two nearby microcapsules. Because this kind of microcapsules is flexible, they are capable of deformation, and the deformed capsules are packed together under the surface tension. Tsapis et al. observed the dynamics of drying droplets of aqueous suspensions of monodisperse carboxylate-modified polystyrene colloids [19]. They found that the viscoelactic deformation and isotropic shrinkage of the shell occur by further drying the colloid. That is to say, at the second step, the ambient microcapsules begin to shrink inward. As the capsules are packed closely at first step, the shrinkage causes the shell of central capsules drive outward, which lead to the yield of the microcapsules. After the water is evaporated entirely, the display thin film coated by gelatin is fabricated with a close package and flatten surface.

Moreover, SEM images are used to identify the drying process of microcapsules. Figure 8a is the image of the capsules dried in water, from which we can see that the microcapsules yield inward, and the leakage of the core material also can be observed. Figure 8b is the image of the capsules dried in gelatin solution, from which we can see that a capsule is pulled to either side of it by ambient capsules as indicated by a circle; this results in the elongation of this capsule, which is consistent with the model illustrated above. By the existence of the gelatin, the capsule can be protected intact, and the film is flat.

Flexibility

To verify the flexibility of the thin film, we carefully exfoliate it from the ITO glass. As discussed above, the film prepared with the binder concentration of 1.0 wt% is of good properties, in this and following experiments, the films used are all fabricated with this concentration. From Fig. 9, we can see that this kind of film is capable of flexibility and can be folded up arbitrarily. The inherent flexibility of the film makes it possible to integrate them into flexible display components. In addition to rigid devices, we also constructed a flexible device by using ITO-coated PET sheet as working electrode and counterelectrode, which also presents good display properties [20].

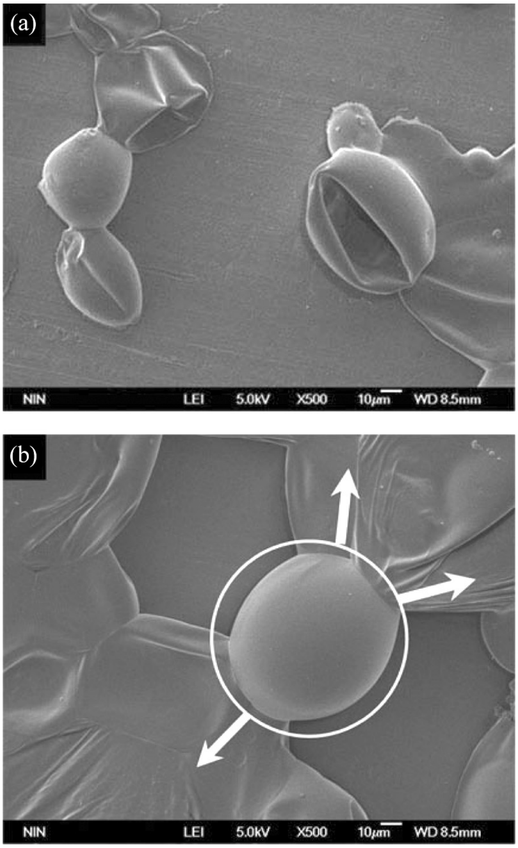


FIGURE 8 SEM images of microcapsules drying in different solution.

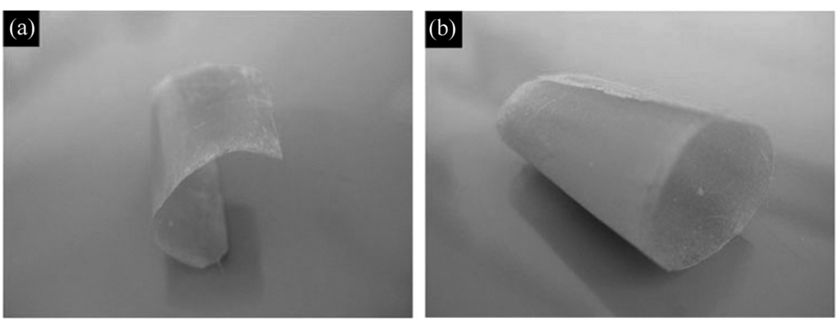
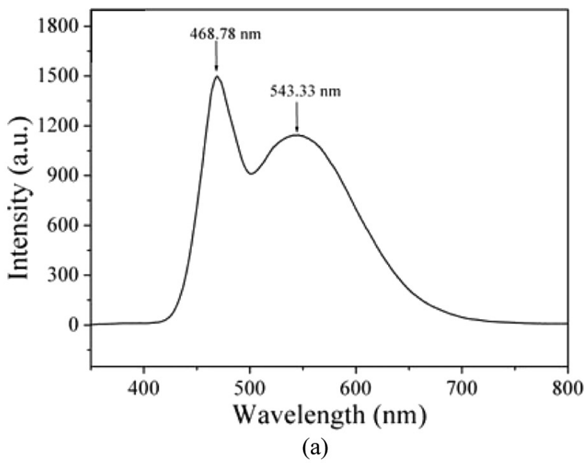


FIGURE 9 Digital picture of display thin film.

Reflective Properties

After drying, the film supported on the ITO glass is sandwiched with the pixel electrode to construct an electrophoretic display. Figure 10a is the luminance spectrum of white lamp house. In this measurement, the incident light is directly faced to the detector. As can be clearly seen, the lamp-house has a maximum at 468.78 nm and secondary maximum at 543.33 nm. In following reflective property measurement, the detector and the incident light are placed at either side of



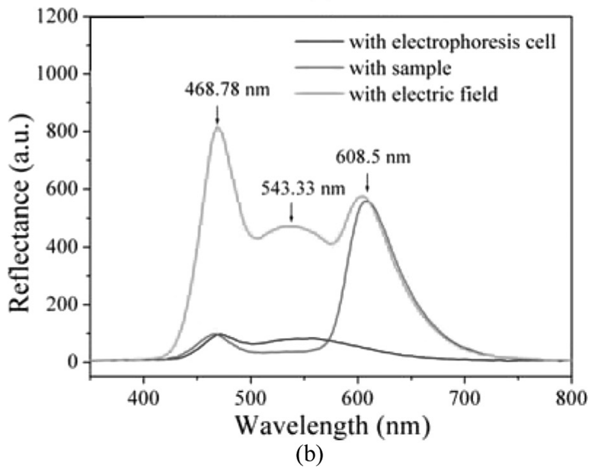


FIGURE 10 Optical properties of display thin film: (a) luminance spectrum of incident light; (b) reflective spectra of EPDTF.

the normal. In Fig. 10b, when an electrophoretic cell without EPDTF is placed, a weak reflective spectrum occurs resulted by mirror reflection of the ITO glass, the shape of the curve is in coincidence with that of incident light (as indicated by blue curve). After the electrophoretic cell with the EPDTF is placed, an intensive reflection with a maximum at 608.5 nm caused by oil red is observed. Herein, the oil red added in core material is used as background of display. Moreover, the weak reflection similar to that of incident light can also be seen (as indicated by the red curve). Once a DC electric field of about ~10 V/μm is applied to electrophoretic cell, a remarkable increase of the reflection appears with a maximum at 468.78 nm and secondary maximum at 543.33 nm (as indicated by the green curve). This can be explained as follows: When the electric field is applied, the TiO_2 particles encapsulated in the microcapsules move to the top of the film and gather there, which is capable of reflecting the incident light. From this, we can see that the EPDTF is of good reflective properties.

Bistability Test

The electrical bistability of this material is also evaluated by applying an initial voltage pulse to display, then disconnecting the electrical leads, and measuring the drift of the peak at 468.78 nm in time. As shown in Fig. 11, the peak sharply decreases at six minutes. After that, it maintains almost unchangeable, which indicates that the

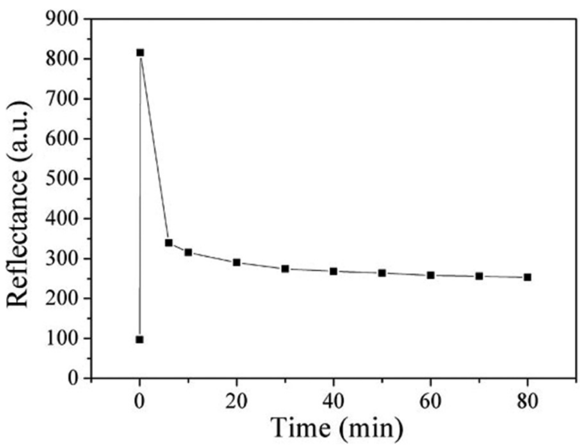


FIGURE 11 Electrical bistability measurement of the EPDTF.

FIGURE 12 Digital picture of static image display.

EPDTF has a high intrinsic bistability, with the peak position stable over an approximately 2-h period.

Static Image Display

To demonstrate the potential of EPDTF, a device is built and tested. In this way, the thin film supported on the ITO glass could be addressed by connecting it in a circuit to the counterelectrode. The digital image of the device in operation is shown in Fig. 12. As can be seen, when a voltage is applied, the school badge of Northwestern Polytechnical University is displayed clearly. This is extremely important for future manufacturing, because the display can be created without the need for drying and separating the microcapsules.

CONCLUSIONS

A kind of electronic ink display thin film, as described in this article, can be fabricated with flatten surface morphology, good flexibility, and reflective property at the binder concentration of 1.0%. In contrast to other display thin film preparation technology, this material can be fabricated without the need for isolating and drying, thereby avoiding the occurrence of the secondary aggregation phenomenon of the capsules and leakage of the core materials. In this way, the electronic ink display exhibits good display properties.

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