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A novel method for the preparation of electrophoretic display microcapsules

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ABSTRACT

The narrow distributed electrophoretic display microcapsules containing electrophoretic ink were prepared using coaxial jet method aided by gas spray. Experimental results showed the size and shell thickness of the microcapsules could be controlled by adjusting flow rates of core and shell fluids as well as gas. The as-prepared white and red microcapsules, with average size of 100 and 200 μm respectively, had high coating ratio (above 90%) and exhibited reversible response to DC electric field. Compared with the approach of other microencapsulation methods, the new technique not only has a simple procedure but also provides a more effective way of size control. This novel method is expected to prepare microcapsules with potential application in the fields of electronic paper and other material science.

1. Introduction

In the past decades, a great deal of attention has been paid to the research of electrophoretic display (EPD) due to its lightweight, low-power, paper-like, flexibility and portability [1–3]. It can be seen in the examples of the microcapsule [4,5] and microcup [2] electrophoretic display, the twisting ball display [6], the cholesteric liquid crystal display [7], and the electrowetting display [8]. Among these different types, the microcapsule electrophoretic display could be the most promising reflective display, as it can offer the advantage of lower manufacturing cost. It is known to be a promising display technology applied in various devices such as e-books and e-newspapers [9,10].

The EPD is based on the movement of charged particles suspended in dielectric fluid caused by applying electric field. In order to improve the stability of the suspension, Jacobson [5] first encapsulated the suspension as electrophoretic microcapsules [11]. Electrophoretic imaging display is based on the movement of pigment particles in a medium that is either clear or in optically contrasting color to the dielectric particles [12]. That is, certain charged particles inside a small capsule can be driven to migrate through the medium toward an electrode with opposite charges. When the voltage of the opposite sign is applied, the observer will see the color change [13,14].

The properties of these microcapsules are the key factors determining the imaging quality. Enhancement of image quality requires EPD microcapsules with very narrow size distribution for precise image control and faster response to the applied driving voltage [15]. So far, various strategies for EPD microcapsules preparation have been proposed, such as in situ polymerization, interfacial polymerization and complex coacervation [16,17]. However, these preparation processes are complicated and difficult to control the size distribution of microcapsules.

Herein a very mild method for the preparation of EPD microcapsules is presented. The method is based on a coaxial jet generating system aided by gas spray, which could fabricate uniform microcapsules under non-reactive conditions in a single step. Influence factors on diameter and shell thickness, such as fluids flow rate and gas flow rate, were investigated. Further, electrophoretic display performance of the as-prepared microcapsules was evaluated.

2. Materials and methods

2.1. Materials

Here the microcapsule containing white or red electrophoretic ink fabrication system is taken for example. Firstly, 1.5 g sodium alginate (NaAlg, CP, Sinopharm Chemical Reagent Ltd) had been dissolved in 100 ml deionized water at 40 °C as shell material.

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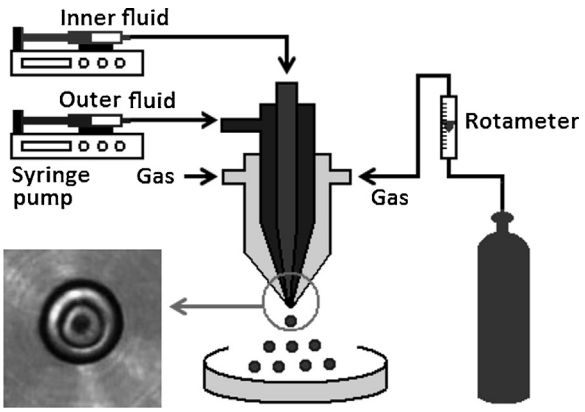

Fig. 1. Coaxial jet device for EPD microcapsules preparation.

The core materials were white or red electrophoretic ink prepared by our laboratory. White E-ink was consisted of TiO_2 nanoparticles (average size 158 nm, ζ-potential 14.27 mV) suspended in tetrachloroethylene (C_2Cl_4). Red E-ink was Pigment Red 2 (P.R.2) nanoparticles (average size 188 nm, ζ-potential −15.83 mV) dispersed in C_2Cl_4 [18]. The microcapsules were collected using 1.5% (w/v) calcium chloride ($CaCl_2$, AR, Beijing Chemical Works) solution.

2.2. Fabrication of EPD microcapsules

Coaxial jet has been previously shown to provide an advantageous means of preparing particles and other special structure particles with a narrow size distribution at ambient temperature and pressure with few fabrication steps [19,20]. Particles whose size ranges from tens of nanometers to several hundred micrometers have been achieved as appropriate for different applications such as pharmaceutical, cosmetic, and food industries and several other technological fields [21,22].

The experimental setup of coaxial jet system is as depicted in Fig. 1. In this setup, a triple nozzle was used. The triple nozzle was assembled by concentrically embedding a coaxial nozzle into a metal gas nozzle. The coaxial nozzle consisted of two stainless steel tubes; the inner and outer diameters (i.d. and o.d.) of the tubes were 0.51 mm (i.d.)/0.82 mm (o.d.) for inner tube, 1.19 mm (i.d.)/1.64 mm (o.d.) for outer tube. The inner tube was supplied with C_2Cl_4, while NaAlg solution was introduced through the outer tube. Two high-precision syringe pumps (KDS-100, KD-Scientific) were used to driven two fluids as well as to control the flow rate of them. The high pressure nitrogen in cylinder was led into the gas nozzle. Two entrances of gas were designed for avoiding swirling. A glass plate filled with about 100 ml $CaCl_2$ solution was kept just below the tip of the compound nozzle. The distance from the tip to the collected plate was fixed at 10 cm during the experiment.

Started two syringe pumps first. Waiting for liquids stably flow out of nozzle and form double layer structure drops, opened the gas valve. As the fluids outflow, the gas exerted force on them. The fluids broke into monodispersed droplets with double layer structure when this force overcame surface tension. When the droplets fell into the collection plate, NaAlg reacted quickly with $CaCl_2$ to produce CaAlg which was insoluble in water. Thus shell solidified and the microcapsules were formed. Subsequently the microcapsules are transferred to a glass beaker, and stir 40 min for full cure. In this study, the influence factors, such as length of the tubes, liquid flow rates, and gas flow rate, were systematically investigated.

2.3. Microcapsules characterization

The diameter and shell thickness of microcapsules were analyzed on an optical microscope (BX41, Olympus, Japan). About 1 ml samples of microcapsules were collected by a dropper pipette and put on a glass slide to obtain microscope image. To determine the mean diameter and shell thickness of microcapsules, at least 100 microcapsules were analyzed from this image. The core material was labeled with Oil Red G (CP, Kewei, Tianjin). After fabricating microcapsules, test the concentration of Oil Red G in receiving liquid by UV spectrophotometer (UV-2501, Shimadu, Japan) to obtain the coating ratio. The microcapsules were collected and put on glass slides with 10% (w/v) Polyvinyl Pyrrolidone (PVP, AR, Beijing Chemical Works) solution. After been dried for 24 h, the movement of charged particles in the microcapsules under DC electric field (E = 30 V/mm) were observed.

3. Results and discussion

It is known from previous work that the size and morphology of the microcapsules can be influenced by the viscosity, density and surface tension of the liquids from which they are formed as well as the processing conditions, i.e., needle size and alignment, liquid flow rates, gas flow rate. The two immiscible liquids, C_2Cl_4 and NaAlg solution were injected with different flow rate combinations and under different gas force to determine the effect upon microcapsules formation. In this study, the microcapsules were only produced when a “stable” jet was achieved, and this was not observed in the absence of the NaAlg solution, indicating that the inner liquid cannot produce a “stable” jet because the viscosity of it was quite low. Hence, the NaAlg solution was the driving liquid because of its higher viscosity compared to C_2Cl_4.

3.1. Positions of inner tube

The position of inner tube should be adjusted according to the properties of different system in coaxial jet process. In this study, three different positions for the inner tube were investigated.

By removing the gas nozzle, the droplets formed on the tip of coaxial nozzle could be easily observed. As shown in Fig. 2a, the tip of inner tube held 0.5 mm axially inside the tip of the outer tube. When droplets fell down because of gravity, it can be easily found that several red cores in one droplet on the tip of coaxial nozzle, because inner fluid was squeezed by the outer fluid due to its low viscosity and surface tension. The prepared microcapsules had multi-core (Fig. 2d) correspondingly. It was obvious in Fig. 2b that the inner tube was 0.5 mm axially extended from the outer. The muti-fluid got separated in the droplets because the density of C_2Cl_4 was greater than that of NaAlg solution, and core tended to sink to the bottom in a muti-fluid droplet. When the droplet exposed to rapid gas flow, the spray process was unstable and the prepared microcapsules did not have core (Fig. 2e). The immiscibility of co-flowing liquid was clearly shown in Fig. 2c, and this was essential for the microencapsulation process when the inner tube and the outer tube were aligned. The inner red-colored fluid was clearly encapsulated by the outer solution. As the gas was led in, the prospective coaxial spray mood formed. In this mode, the droplets broke up into particles below the triple nozzle. By using this setup, microcapsules with good morphology and high coating ratio were prepared (Fig. 2f).

3.2. Effect of inner flow rate

In order to obtain monodispersed microcapsules, the liquid flow rates in the inner and outer tubes were key control parameters. Gas