Ultraviolet-assisted microfluidic generation of ferroelectric composite particles

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We report on the feasible fabrication of microfluidic devices for ferroelectric polymers' synthesis in a rapid and stable fashion. Utilizing micro-mixing and flow-focusing in microchannels, poly(vinylidene fluoride-trifluoroethylene) and copper phthalocyanine are uniformly dispersed in one hydrogel particle, which are then demonstrated to immediate and complete on-chip steady polymerization by moderate ultraviolet treatment. The advantage of our droplet-based microfluidic devices is generating versatile particles from simple spheres to disks or rods, and the lengths of particles can be precisely tuned from 30 to 400 μm through adjusting the flow rates of both disperse and oil phases. In addition, this mixed technique allows for the continuous production of dielectric microparticles with controlled dielectric properties between 10 and 160. Such a microfluidic device offers a flexible platform for multiferroic applications. © 2016 AIP Publishing LLC.
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I. INTRODUCTION

Microfluidics has grasped much attention recently in biological analysis,¹ chemical synthesis,² drug delivery,³ thermal sensor,⁴ and hydrodynamic mechanisms⁵ due to its advantages of low fabrication cost, minimal materials' consumption, and fast continuous processing.^{6,7} Among various microfluidic technology that have been developed, microreactor systems are becoming increasingly popular for fabricating materials.^{8,9} Compared to conventional batch reactions, the microreactor shows unique advantages such as continuous processing and highly controlled reaction conditions.² As a crucial component in a microreactor device, micromixers play a crucial role in fully mixing of different reagents. The chaotic advection generated in the twisted structure of micromixer guarantees the two dispersed phases fully mixed.¹⁰ The microreactor systems are now able to produce a diverse array of multifunction metal nanoparticles.^{11–13} However, the generated nanoparticles are characterized by tableting, which have no substantive differences from traditional bulk or film. And the generated nanoparticles are usually used for preparing macroscopic device but rarely applying in microscopic device.

To overcome the above limitations, droplet microfluidics technology is taken into consideration for its capability of generating diverse microparticles from simple spherical particles, disk-like to rod-like particles.^{14,15} Moreover, through adjusting the throughputs of the liquids injected into the microdevice, the resultant microparticles with different diameters and ratios of compositions can be conveniently realized.¹⁶ Additionally, the particles generated by droplet-microfluidics exhibit much better uniformity in size distribution than those synthesized by traditional method.¹⁷

Herein, we introduce a continuous generation method of poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE))-copper phthalocyanine (CuPc) dielectric microparticles with different morphologies (spheres, disks, and rods) based on the droplet-microfluidic technique. P(VDF-

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TrFE), as a ferroelectric polymer, has been widely used in actuators, sensors, artificial muscles, high charge-storage capacitors, and microfluidics due to their portability, high mechanical elasticity, and sensitive strain levels.^{18–23} Compared to other ferroelectric materials, P(VDF-TrFE) exhibits a relatively high room-temperature dielectric constant and high electric energy density, and thus has been thoroughly studied.^{24–26} As a filler blended into the matrix, CuPc oligomer with a very high dielectric constant ($>10^5$) has been widely studied.^{27,28} After blended with this filler, the resultant composite gains a dramatic enhancement of the electrostriction and dielectric constant because of the exchange coupling at the interface of CuPc and copolymer matrix.^{29,30}

Compared with the conventional methods generating similar composite materials, our system of microreactor and droplet microfluidics makes it feasible to prepare morphology-controlled particles. This technique allows for the continuous production of dielectric microparticles with steerable dielectric properties, which would be difficult to achieve through the current batch technique. The P(VDF-TrFE)-CuPc microparticles generated by our device are demonstrated to immediate and complete on-chip polymerization by UV-cured process. The rapid UV-cured process makes it possible to generate the stable structure with little deformation. The size of the generated particles is uniform and can be precisely controlled by modulation of the flow rates and the structures of micro-channel. And they have the potential for micro devices.

II. MATERIALS AND METHODS

A. Microfluidic device design and fabrication

The schematic of droplet-based microfluidic device is shown in Fig. 1(a). The device is mainly made of one micromixer to blend the two dispersed phases, one flow-focusing channel to generate composite droplets, and one straight channel to polymerize the droplets to particles when exposed to UV-light. The width of the inlet channels and the flow-focusing channels was at first $200\ \mu\text{m}$ and then tapered to $50\ \mu\text{m}$ near the orifice. When the height of the channel is $50\ \mu\text{m}$ equaled to the orifice, the spheres were generated at the orifice due to the minimization in interfacial energy. While when the height is about $25\ \mu\text{m}$, the disks were produced under the compress of the channel. And the rods could be acquired from the deformation at the narrow appeared on the straight channel.

As shown in Fig. 1(b), we made the relief structures of the microchannels by photolithography using SU-8 2050 photoresist (Microchem Corporation, MA, USA) on a silicon wafer. Then, we gained the poly (dimethylsiloxane) (PDMS, GE Toshiba Silicone Corporation, Ltd.,

FIG. 1. (a) Schematic diagram of the microfluidic setup used for the generation of P(VDF-TrFE)-CuPc composite particles. (b) Photograph of the microfluidic device.

USA) layer from the relief structure using a conventional soft lithography technique.³¹ After that, the PDMS channels were treated with oxygen plasma (PDC-32G, Harrick plasma, USA) to form silanol groups to bond to a glass substrate. Eventually, the microchip was cured at 120 °C for 72 h to regain hydrophobicity.

B. Reagents and materials mixing processing

In our microfluidic flow-focusing device, the soybean oil (Beiya Medical Oil Corporation, Ltd., China) was prepared as the continuous phase. The P(VDF-TrFE) powders (70/30 ratio, Piezotech, France) were dissolved in dimethylformamide (DMF, National Medicines, China) typically at 8 wt. % as a dispersed phase. The CuPc dielectric particles (National Medicines Corporation, Ltd., China) resuspended in DMF at 5 wt. % as another dispersed phase. Because of the infusibility of P(VDF-TrFE) in water, the DMF was chosen as the solution, and the UV-cured was selected as solidification.³² Both of the dispersed phases were added to 34% (v/v) poly(ethylene glycol) diacrylate (PEG-DA, Sigma Aldrich, St. Louis, MO, MW ~ 575, $\rho = 1.12$ g/ml, $\mu = 70$ cP) as a photocurable monomer and 6% (v/v) 2-hydroxy-2-methylpropio-phenone (Darocur 1173, Sigma Aldrich, St. Louis, MO, MW = 164.2, $\rho = 1.077$ g/ml, $\mu = 25$ cP) as a photoinitiator for UV-initiated polymerization.³³ The two dispersed phases were then injected into the microchannels independently using syringe pumps (TS2-60, Longer Precision Pump Corporation, Ltd.) to form parallel laminar flow in the upstream channel (Fig. 2(a)) and got mixed in the S-shape reagent mixing channel (Figs. 2(b)–2(e)). The chaotic advection generated in the twisted structure guaranteed the two dispersed phases fully mixed.¹⁰

C. Droplets generation, polymerization, and on-chip observation

After mixing, the homogenous mixed solution was sheared off into anisotropic droplets by the oil phase at the flow-focusing orifice (Fig. 2(f)).³⁴ The size of the hydrogel beads could be controlled from tens to hundreds of micrometers in diameter by regulating the flow rates of fluids. Moreover, the feature of the generating particles could be tuned by the confined polymerization. Compared to spherical particles, the diverse microstructures could have new applications in field of microcircuits, condensed matter physics, and materials chemistry.³⁵ The shape is determined by the relationship between the diameter d of the droplets, the width w , and the height h of the microchannel. For example, when $w > d$ and $h < d$, the droplets acquire a disk-like shape. In contrast, when $w < d$ and $h < d$, the droplets assume a rod-like shape. And then,

FIG. 2. P(VDF-TrFE) and CuPc solutions were merged into the microchannel (a) and well mixed in the following S-shape (b)–(e) channel. (f) Droplets were generated in the flow-focusing manner. (g) The optical intensity analysis of the merging solution from C1 to C5 in the mixing channel with a certain mixing ratio. (h) Mean volumetric ratio of CuPc dispersed in the composite (on the right) was tested by the optical intensity of final solution (on the left).

the various droplets were solidified when exposed to UV-light in the straight channel.³⁶ Due to the microsize of droplets and the high energy flux provided by the UV lamp, the droplets polymerized within very little exposure time ($<1\ \mu\text{s}$).³⁷ As the UV-cured process was rapid and stable, we should focus the UV light onto a specific location near the outlet to avoid blocking. The generation of particles in the microchannel was recorded with a charge coupled device camera (DP 72, Olympus, Japan) on an inverted fluorescence microscope (IX71, Olympus, Japan). The images are analyzed by Image-Pro Plus 6.0 software to detect the optical density at one spot and quantify relative parameters of generated droplets and polymerized particles. Following the generation process, the diverse particles were transferred into a centrifuge tube at the outlet and then centrifuged in *n*-hexane (China National Medicines Corporation, Ltd., China) to remove the oil for three times.

III. RESULTS AND DISCUSSION

A. Concentration control and detection

In our experiments, we achieved the concentration of the mixed flow through the optic analysis of the acquired images. To detect the efficiency of mixing of the two reagents in the S-shape mixing channel, the optical density along the lines perpendicular to channels was measured.³⁸ We choose five detection lines (C1–C5) which perpendicular to mixing channel to observe whether the two reagents were completely mixed (Figs. 2(b)–2(e)). The optical density along the lines was measured by subtracting the background optical density from the reagent optical density. Then, we got the optical density curves in the range of different spots along the detection lines. As shown in Fig. 2(g), on the line C1, the distribution of optical density was nonuniform. From C1 to C5, the optical density got more and more smooth and steady. Finally, the resultant optical density across the channel was almost the same at C5, which meant the two reagents were completely mixed.

The theoretical calculation was carried out for optic analysis. The final concentration of CuPc content could be expressed as

$$\eta = \frac{V_{o-f}}{V_{o-f} + V_{b-f}} = \frac{V_{o-f}/t}{V_{o-f}/t + V_{b-f}/t} = \frac{U_{o-f}}{U_{o-f} + U_{b-f}}, \quad (1)$$

where V_{o-f} and V_{b-f} are the volume of original CuPc and P(VDF-TrFE) phases. And U_{o-f} and U_{b-f} denote flow rate of original CuPc and P(VDF-TrFE) phases. According to Equation (1), we could modulate CuPc concentration by changing the flow rates of P(VDF-TrFE) and CuPc phases.

To characterize the final concentration of CuPc before droplet generation, different volumetric ratios were tested by the optical density at the end of mixed channel. As shown in (Fig. 2(h)), it can be seen that the optical density is increased with the increasing volumetric ratio of CuPc dispersed in the composite.

B. Particle morphology

The synthesized spheres, disks, and rods were shown in Figs. 3(a)–3(c). The cured gel-particles were stable and uniform. To further analyze the microstructure morphology of these particles, scanning electron microscope (SEM HITACHI S4800) (Figs. 3(d)–3(f)) was performed. A magnification of the rods (Fig. 3(g)) was inserted to show the surface morphology of the rod. These high magnification images confirm that it is feasible to prepare versatile functional micro particles based on the droplet-based microfluidics. Moreover, the sizes of particles could be precisely controlled by modulating the two dispersed phases and the continuous phase. Utilizing this method, the diameters of spheres and disks could be changed from 30 to 100 μm . And the lengths of the rods, which formed from the deformation of spheres under confinement of the channel, could be modulated from 70 to 400 μm (Fig. 3(h)). A mount of 20 rod-like

FIG. 3. Optical microscopy images of collected composite particles of spheres (a), disks (b), and rods (c), respectively. SEM images of the particles of spheres (d), disks (e), and rods (f), respectively. The inset picture (g) is the enlarged surface of the rods. (h) The relationship between mean diameters of rod-like droplet (black lines)/particles (red lines) and flow rate of dispersed phase/oil phase. Left: Mean diameters changed with the flow rate variation of dispersed phase under the flow rate of oil phase fixed at 194 $\mu\text{L/h}$. Right: Mean diameters were controlled through adjusting the flow rate of oil phase, with the flow rates of two dispersed phases both fixed at 49 $\mu\text{L/h}$.

droplets/particles were counted to provide average length and relative error bar. It can be seen that the length is a bit shorter than the droplet, showing that the droplets shrunk after gelation.

C. FTIR, XRD, and dielectric constant characterizations

Subsequently, the collected samples were dried at 120 $^{\circ}\text{C}$ for 12 h and subsequently annealed at 135 $^{\circ}\text{C}$ for 2 h.³⁹ After that, Fourier transform infrared spectroscopy (FTIR, Nicolet Is10, USA), X-ray diffraction (XRD, D8 Advanced), and dielectric constant were used to characterize the dried P(VDF-TrFE)-CuPc composite particles in Fig. 4. The FTIR spectra of CuPc powder, P(VDF-TrFE) UV-cured particles, and P(VDF-TrFE)-CuPc composite UV-cured particles were shown in Fig. 4(a). The strong absorption peaks at 840 cm^{-1} , 1280 cm^{-1} , and 1431 cm^{-1} are characteristics of polar β -phase bands of P(VDF-TrFE), which plays an important role in the relaxation process in the crystalline region of the copolymer. And that is the reason in enhancing the dielectric property of one material. And in the spectra of CuPc powder, the absorption peaks at 730 cm^{-1} , 772 cm^{-1} , 797 cm^{-1} , 920 cm^{-1} , 990 cm^{-1} , 1060 cm^{-1} , 1090 cm^{-1} , and 1129 cm^{-1} are attributed to the resonance of aromatic hydrogen in CuPc. The peak at 920 cm^{-1} is the most important characteristic peak of CuPc which confirms the resonance of Cu-N bond. By analyzing the result, the spectra of P(VDF-TrFE)-CuPc UV-cured composite particles show no distinct peaks except a new peak at 730 cm^{-1} which is from the characteristic peaks of CuPc powder. It is estimated that the process in the micromixer is a blend of CuPc and P(VDF-TrFE) solution rather than a chemical reaction.

XRD pattern measurements were performed at room temperature to investigate the typical crystal structures of the composite particles, as shown in Fig. 4(b). In the spectra of P(VDF-TrFE) UV-cured particles, the diffraction peak observed at 19.8° corresponds to (200, 110) reflection of the β -phase P(VDF-TrFE) polymer matrix, and there is no other remarkable peaks in this pattern, which confirms that the UV-cured agents PEG-DA and Darocur 1173 are not crystallite. Moreover, all the diffraction peaks of CuPc can be readily indexed, which are in good agreement with JCPDS No. 37-1846. For the composites, the plane (312) arising from the CuPc crystalline phase can be used to distinguish the P(VDF-TrFE)-CuPc composite particles

FIG. 4. (a) FTIR spectrum of (I) pure CuPc powder, (II) P(VDF-TrFE) UV-cured particles, and (III) P(VDF-TrFE)-CuPc composite UV-cured particles. (b) XRD patterns of (I) P(VDF-TrFE) UV-cured particles, (II) pure CuPc powder, and (III) P(VDF-TrFE)-CuPc composite UV-cured particles. (c) Dielectric constant of the samples with seven concentrations of CuPc with percentages of 0%, 1.31%, 1.75%, 2.6%, 5%, 9.6%, and 13.8% in the range of 1 kHz to 100 kHz.

from pure P(VDF-TrFE) particles. Furthermore, neither a new peak can be found in this pattern except for those of P(VDF-TrFE) and CuPc, which indicates that no new phase produced in the composite.

In addition, to investigate the dielectric properties of P(VDF-TrFE)-CuPc composite particles, gold point electrodes ($0.5\text{ mm} \times 0.5\text{ mm}$ in size) were deposited on the samples using magnetron sputtering machine (FJL 560, Shenyang Keyi Co., China). The frequency dependent dielectric constant ε was obtained through capacitance (C) measurements by the Impedance Analyzer (JP2 KG00683, Japan) according to the relationship of dielectric constant ε and capacitance C : $\varepsilon = Cd/(\varepsilon_0 s)$, where ε_0 is the vacuum dielectric permittivity, d is the thickness of the sample, and s is the square of the gold point electrode. Fig. 4(c) shows the dielectric constants of P(VDF-TrFE) UV-cured particles' sample of CuPc with percentages of 0%, 1.31%, 1.75%, 2.6%, 5%, 9.6%, and 13.8% in the range of 1 kHz to 100 kHz, respectively. As generally expected, the dielectric constants of composites are much higher in comparison to pure P(VDF-TrFE) UV-cured particles. Generally, at lower frequency, the samples present a higher dielectric constant. What's more, even at high frequencies, the dielectric constant of composite samples is still relatively high than that pure P(VDF-TrFE). The dielectric constant value of composite samples is increased with increasing concentration of CuPc, indicating the contribution of CuPc to the enhancement of the dielectric properties of the composite samples. The nonlinear variation of the curves could be explained by the interference of the UV-cured adjuvant during CuPc and copolymer matrix exchange coupling process.

IV. CONCLUSION

In summary, we demonstrate a system of micro-mixing and flow-focusing technique for morphology-controlled P(VDF-TrFE)-CuPc particles' (spheres, disks, and rods) synthesis in a rapid and stable fashion. The subsequent UV-cured process guarantees the resultant particles polymerized with little deformation. Utilizing this method, the resultant microparticles can be precisely controlled between 30 and $400\text{ }\mu\text{m}$ by modulation of the flow rates and the structures of micro-channel. Moreover, this technique allows for the continuous production of dielectric microparticles with controlled dielectric properties from 10 to 160. The relatively simple and economical device has promising potentials in multiferroic fields.

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