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Inkjet Printing Microcapacitors for Energy Storage

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Abstract—Micro energy storage devices are appealing, and highly demanded for diverse miniaturized electronic devices, ranging from microelectromechanical system, robotics, to sensing microsystems and wearable electronics. However, making high-energy microcapacitors with currently available printing technologies remains challenging. Herein, we show the possibility to use latex polyvinylidene fluoride (PVDF) as aqueous ink for making dielectric capacitors on the microscale. The dielectric properties of printed microcapacitors can be optimized based on a novel approach, i.e., mixing PVDF latex with polyvinyl alcohol (PVA) to realize dielectric organic nanocomposites. The PVA prevents the coalescence of PVDF nanoparticles and serves as a continuous matrix phase with high dielectric breakdown strength. While the well-dispersed PVDF nanoparticles serve as highly polarizable and isolated domains, providing large electric displacement under high fields. Consequently, a high discharged energy density of 12 Jcm⁻³ is achieved at 550 MVm⁻¹.

I. INTRODUCTION

The emerging micro-energy storage devices provide excellent micro-scale peak power. They can be easily integrated into miniaturized electronic devices, such as energy-harvesting microelectromechanical system, microrobotics, and sensing microsystems.[1,2] Micro-batteries and micro-supercapacitors represent newly developed miniaturized electrochemical energy storage devices. They have high gravimetric energy density but fall short of the rising demands of rapid charging/discharging and high cycling for the next-generation of micro-energy storage devices. Electrostatic capacitors are the only energy storage methodology with intrinsically high power density. They are appealing for reliable and efficient electric microsystems. However, the printed dielectric capacitors have a low energy density that is approximately three orders of magnitude less than printable microsupercapacitors.[3] Today, this drawback leads to large printing area and high system weight. Therefore, developing new printable microcapacitors with improved energy density is imperative to enable the reduction of size, weight, and cost of the modern printing power electronics.

To date, most of the microcapacitors have been realized by inkjet depositing droplets of ceramic nanopowder suspensions or polymer dielectric inks.[4-6] In particular, films of high-*k* metal oxides have been printed. However, these films are brittle and need post annealing treatments. As alternatives, polymeric materials are more appealing due to their low-temperature processing, high breakdown strengths, and low losses.[7-9] However, the low dielectric constants usually give rise to a low energy density (<3 Jcm⁻³).[9] Today, inkjet-printed microcapacitors with superior energy storage performances have not been realized yet.

Herein, we report a high-energy microcapacitor fully inkjet-printed on a poly(ethylene naphthalate) (PEN) substrate. The devices are made from water-based inks, a mixture of PVDF latex particles and water soluble PVA. The mixture is printed as dielectric layers sandwiched between two carbon nanotube (CNT) electrodes, which are also deposited by inkjet printing water-based CNT inks. The capacitance of printed microcapacitors can be tuned through the thickness of printed dielectric layers. The obtained microcapacitors show high flexibility and stable capacitance even under large bending deformation. In addition, the microcapacitor displays a discharged energy density as high as 12 Jcm⁻³. This value represents an improvement of 400 % as compared to films formulated with single PVDF or single PVA components. The environmentally friendly water based inks coupled with the superior energy storage performances of printed dielectrics makes our microcapacitors promising for demanding printed electronics that require micro-scale peak powers.

II. RESULTS AND DISCUSSIONS

As schematically demonstrated in Figure 1, three steps were involved to print a microcapacitor. We first inkjet deposited the bottom electrode using CNT water inks. After completely drying, a dielectric layer of PVDF/PVA nanocomposite will cover this electrode and an additional top electrode will be deposited at the end to form a sandwiched capacitor structure. The PVA prevents the coalescence of PVDF nanoparticles and serves as a continuous matrix phase with high dielectric breakdown strength. While the well-dispersed PVDF nanoparticles serve as highly polarizable and isolated domains, providing large electric displacement under high fields.

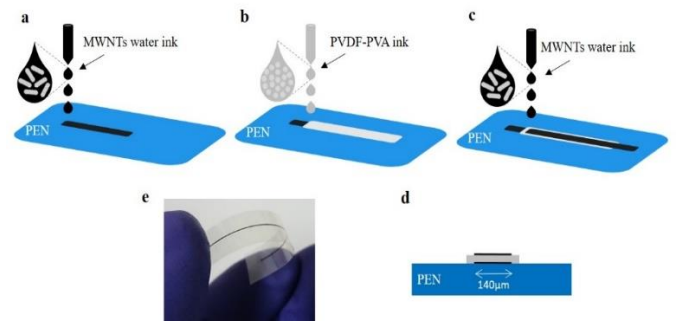


FIGURE 1. (a) Bottom electrode printed on PEN substrate using CNT water ink. (b) PVDF-PVA ink printed on the top of the bottom electrode, serving as a dielectric layer. The mass ratio between PVDF and PVA in the inks is 93:7. (c) Printing top CNT electrode on top of the dielectric layer. (d) Lateral view of the designed microcapacitor with an effective electrode width of around 140 μm. (e) Photograph of bent microcapacitor with an effective area of $\sim 2.8 \times 10^{-6} \text{ m}^2$.

We first characterize the low-field capacitive behaviors. The thickness of the dielectric layer can be tuned at will by changing the printing passage numbers and the drop spacing. So with a given electrode size, the capacitance changes with the printing layer numbers (Figure 2a). However, we found that the dielectric constant and losses do not change with the printing parameters (Figure 2b).

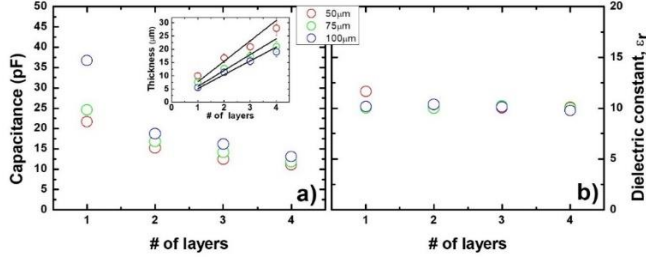


FIGURE 2. (a) Tailored capacitance of the printed microcapacitors. (b) The dielectric constant of printed PVDF/PVA nanocomposite as a function of printing passage numbers.

However, at high electrical fields, the breakdown strength increases with the layer number and reaches 570 MV/m for four layers of PVDF/PVA composites (Figure 3a). This breakdown strength is much higher than that of pure PVDF latex films, and remains comparable to the pure PVA films. The four-layer PVDF/PVA nanocomposite enjoys high polarization of a maximum charge density of 55 mC/m^2 at 550 MV/m (Figure 3b). The hysteresis of the P - E loop increases slowly with the applied electric field. These two features lead to a large discharged energy density of 12 J/cm^3 , and an efficiency of 78% (Figure 3c-d). This energy density exceeds those of the pure PVDF materials already reported in the literature. It is also six times higher than pure PVDF latex and pure PVA printed with the same four layers.

III. CONCLUSION

We used a low-cost and environmentally friendly water-based PVDF latex to achieve high-energy and high-efficiency miniaturized capacitor with inkjet printing technology. The achieved performances are much higher than that of pure PVDF latex, and PVA. The PVA not only allows a homogeneous film to be obtained, but also improves the breakdown strength of the polymer mixture. The obtained systems are compact polymer with few defects, which results in a higher discharged energy density and high efficiency.

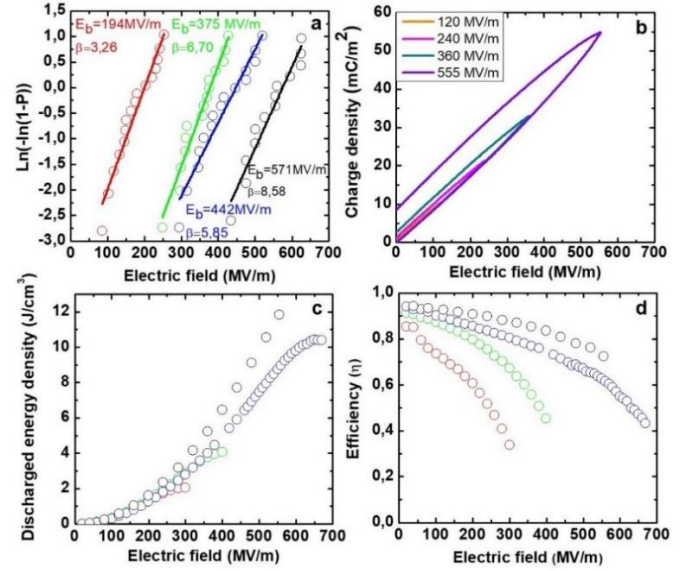


FIGURE 3. (a) Cumulative failure probability distribution. (b) P - E loops of microcapacitors printed with four printing layers. (c) Discharged energy density and (d) charge/discharge efficiency of microcapacitors as a function of the electric field. (a-d) 1 PVDF/PVA layer (Red), 2 layers (Green), 3 layers (Blue), and 4 layers (black).

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