Journal of Metals, Materials and Minerals, Vol. 30, No. 4, pp. 39-44, 2020

Screen printed textile electrodes using graphene and carbon nanotubes with silver for flexible supercapacitor applications

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Received date:
26 June 2020
Revised date
11 August 2020
Accepted date:
23 August 2020

Keywords:
Screen printing;
Graphene;
CNT;
Cotton;
Flexible supercapacitor

Abstract

The eco-friendly conductive cotton textile is promising alternatives for the flexible substrates in wearable devices since the cotton is as an inexpensive natural fabric material and compatible in modern portable electronics with adequate electrical conductivity. In this work, flexible conductive cotton-based electrodes are prepared via a screen-printing method using the carbonaceous nanomaterials such as carbon nanotubes (CNTs) and graphene with an additional component of conductive silver (Ag) powder and textile ink. The prepared conductive cotton electrodes exhibit lower sheet resistance (< 10 Ω) along with superior mass loading (20-30 $mg \cdot cm^{-2}$). On the basis of the performance of cotton electrodes prepared, an all-solid-state flexible supercapacitor device was successfully fabricated which exhibits a high specific areal capacitance of 677.12 $mF \cdot cm^{-2}$ at 0.0125 $mA \cdot cm^{-2}$ for a suitable electrode composition (60% of Ag and 40% CNTs) using a PVA-KOH gel electrolyte. The flexible device endures a stable electrochemical performance under severe mechanical deformation using different bending angles (0°, 30°, 45°, 60° and 90°) of the device and possesses excellent cyclic stability with the capacitance retention of ~80% even after 3000 CV cycles.

1. Introduction

Wearable electronics and smart textiles are a kind of modern generation textiles for a wide variety of applications in various fields such as medicine, defense, sensors, data processing and storage devices [1,2]. The development of flexible energy storage devices with a lightweight compact design including high power and high energy density materials are inevitable [2-7]. The flexible supercapacitors can be divided into two major types such as electric double-layer capacitors (EDLCs) and pseudocapacitors (PCs) [4,8-10]. The EDLCs store electrical energy through a non-faradaic electrostatic reaction mechanism of charge accumulation at the electrode/ electrolyte interface. In general, carbon-based nanomaterials exhibit EDLC characteristi due to a high specific surface area for the reversible charge adsorption or storage with excellent cyclic stability [6,8]. The recent research efforts are extensively devoted to developing conductive-based textiles because of a demand for the huge market potential for wearable smart gadgets [11]. In this regard, cotton is considered as the ''green'' textiles which can be effectively applied in the modern portable electronics with sufficient electrical conductivity owing to its adaptability for better flexibility, comfortableness, easy breathability, high stretching ability, eco-friendliness and inexpensive nature compared to synthetic fabrics [12,13].

Nevertheless, the key challenges are mainly due to the conversion of ordinary cotton textiles into an electrically conductive cotton material. So far, various coating techniques were attempted for fabricating the conductive cotton textiles such as carbonizing [14-16], dip-coating [2,4], electroless silver plating [11], and chemical silver plating [17]. Moreover Zhang et al. demonstrated activated textile carbon (aTC) network via carbonization and chemical activation [18]. Zhang *et al.* fabricated by depositing polypyrrole (PPy) nanotubes and Zr-based MOF (UiO-66) particles on cotton fabrics [19]. Paleo *et al.* developed hybrid solid-state supercapacitors based on the AC and MnO_2 coated cotton fabrics using two different solid electrolyte (Nafion and Aquivion) [20]. Oje *et al.* used a radio frequency (RF) sputtering to fabricate silver (Ag) film on textile fabrics [21].

Subsequently, the earlier investigation of fabricating the conductive-based cotton textiles using the activated carbon sources demonstrated promising results for designing innovative flexible supercapacitors [22]. In this study, the flexible conductive cotton textiles are successfully developed and exclusively investigated for using different proportions of silver and carbon-based nanomaterials (MWCNTs and graphene with a textile ink as binder via a simple screen-printing process. Moreover, the solid-state symmetric flexible supercapacitor device was well-constructed using a high-performance electrode composition identified with a solid-gel electrolyte (PVA-KOH). The fabricated

 DOI: 10.14456/jmmm.2020.49

flexible device exhibits the remarkable areal specific capacitance of 677.12 mF·cm^{-2} at the current density of 0.0125 mA·cm^{-2} and excellent cyclic stability, outstanding flexibility under vigorous bending angles of the device leading to its potential applications in wearable devices.

2. Experimental

2.1 Materials

Cotton fabrics were obtained from the local market in Bangkok, Thailand. Carbon nanotubes (CNTs) for MWCNTs, 30-50 nm, Purity~95%, length 0.5-2 µm - XFNANO INC (China); Graphene (JCGNP-50-9), thickness < 15 µm, film size 3-6 µm, purity > 98% - Nanjing FAME Bearing Co. Ltd. (China); Silver (Ag) powder - Wuxi Adams technology Co., Ltd (China); Textile Ink - Normal Lemon yellow 1006-(SCALA 99) - Scala Screen & Digital Co., Ltd. (Thailand); Potassium hydroxide (KOH) and Sodium hydroxide (NaOH) - CARLO ERBSA; Polyvinyl alcohol (PVA) - Shanghai Titan chem Co. Ltd. (China).

2.2 Preparation of conductive screen print cotton (CSPC)

The preparation process of conductive screen print cotton (CSPC) is illustrated as shown in Figure 1, which is based on the earlier method reported elsewhere [22]. The cotton fabrics were immersed in 1 M NaOH solution and boiled at 95°C for 1 h; washed with deionized water to remove any undesirable impurities such as oil and dust until getting neutral pH of the wet cotton and dried in a vacuum oven at 60°C overnight. The conductive coating ink was prepared using silver powder (Ag), textile ink, carbon nanotubes, or graphene in different proportion and screen printed on the cotton and dried under vacuum condition. The prepared CSPC specimens were denoted as 8AC, 6AC, 8AG, 6AG, 631AGC, 622AGC and 613AGC (where A stands for Ag; C for CNTs and G for graphene) according to the different volume ratio of the coating composition (Table 1). The mass loading of obtained samples are also listed in Table 1.

2.3 Characterization techniques

The surface morphologies of the CSPC specimens were observed by using a scanning electron microscope (SEM; Hitachi-S4800). The symmetric two-electrode cell setup was employed for the galvanostatic charge-discharge (GCD) cycles using a Neware multi-channel battery system (Shenzhen, China) at different current densities of 0.10 to 2.5 mA·cm^{-2} in 6 M KOH electrolyte. The fabricated flexible supercapacitor device was characterized in a two-electrode system using cyclic voltammetry (CV) and GCD techniques using the Palmsens-4 instrument. The digital palm-size multi-meter (UNI-T; UT33C+) was used to measure the electrical resistance of the conductive cotton textiles.

Table 1. Composition of the conductive coating ink prepared in different volume ratio using silver powder (Ag), carbon nanotubes (CNTs) and graphene.

Sample Name	Ag (vol%)	Graphene (vol%)	CNTs (vol%)	Mass loading (mg·cm^{-2})
8AG	80	20	-	23.55±4.61
6AG	60	40	-	25.71±4.97
8AC	80	-	20	26.56±4.19
6AC	60	-	40	24.40±4.59
631AGC	60	30	10	28.11±8.17
622AGC	60	20	20	24.69±7.22
613AGC	60	10	30	20.60±3.75

3. Results and discussion

Figure 1(a-h) depicts the fabrication procedure of the conductive cotton electrodes during various stages using the coating composition of silver, carbon nanotubes and graphene nanosheets with textile ink as a binder. As can be seen from Figure 1(e,h), the carbon nanomaterials of CNTs and graphene nanoflakes can be successfully coated onto the cotton textile for the flexible conductive sheet substrates. It was found that the thickness of the prepared CSPC did not vary significantly (~0.1 mm thick) after the coating paint was applied onto it through screen-printing. The mass loading of the active material of the CSPC was found to be 20-30 mg·cm^{-2}. The resistance of CSPC specimens prepared with CNTs such as the composition of 8AC and 6AC species revealed the resistance of 7.13±2.61 and 6.82±3.28 Ω, respectively. The resistance value decreases when extra CNTs powder was added due to increased electrical conductivity. Similarly, the resistance of the CSPC specimens fabricated with graphene nanosheet (8AG and 6AG) decreases when an additional amount of graphene was added. However, the slight declining tendency of the resistance value was observed for graphene-coated CSPC compared with that of CSPC prepared with CNTs, indicating a better electrical conductivity of the CNTs in the coating composition. On the contrary, the mixed composition of graphene with CNTs can cause higher resistance as the extra amount of graphene was added resulting in the restacking of graphene nanosheets leading to agglomeration which can cause for the increased sheet resistance.

The galvanostatic charge-discharge (GCD) measurements were executed to investigate the electrochemical properties and specific capacitance values for the various types of conductive cotton electrodes fabricated with different concentrations of carbon sources of CNTs, graphene as well as the mixture of CNTs and graphene. The textile ink with silver powder was used as the common coating ink resources along with the carbon-based active materials. Figure 2(a-c) shows the GCD profiles of the CSPC electrodes fabricated for the various active components of CNTs, graphene and the mixed composition of CNTs and graphene, respectively. The calculated spatial specific

capacitance values at different current densities are shown in Figure 2(d). As can be seen from Figure 2(d), the areal specific capacitance values were increased when the addition of more amount of CNTs and graphene powder. Among all specimens of the CSPC electrodes prepared, the enhanced areal specific capacitance values were observed with an increased volume ratio of CNTs. The obtained results can be confirmed by comparing the GCD electrochemical data of 631AGC and 613AGC specimens. The specific capacitance was remarkably increased when the concentration of CNTs alone increased. The improved electrochemical performance of the electrode obtained among all the prepared CSPC specimens is identified for the specific composition of the sample 6AC (i.e., 60% silver + 40% CNTs) which exhibits an ideal rate capability of 50-75 $mF \cdot cm^{-2}$ at the current densities of 0.1 to 2.5 $mA \cdot cm^{-2}$ in 6M KOH electrolyte. The suitable electrode composition was further opted to fabricate an all-solid-state flexible supercapacitor device with a solid gel electrolyte (PVA-KOH) system.

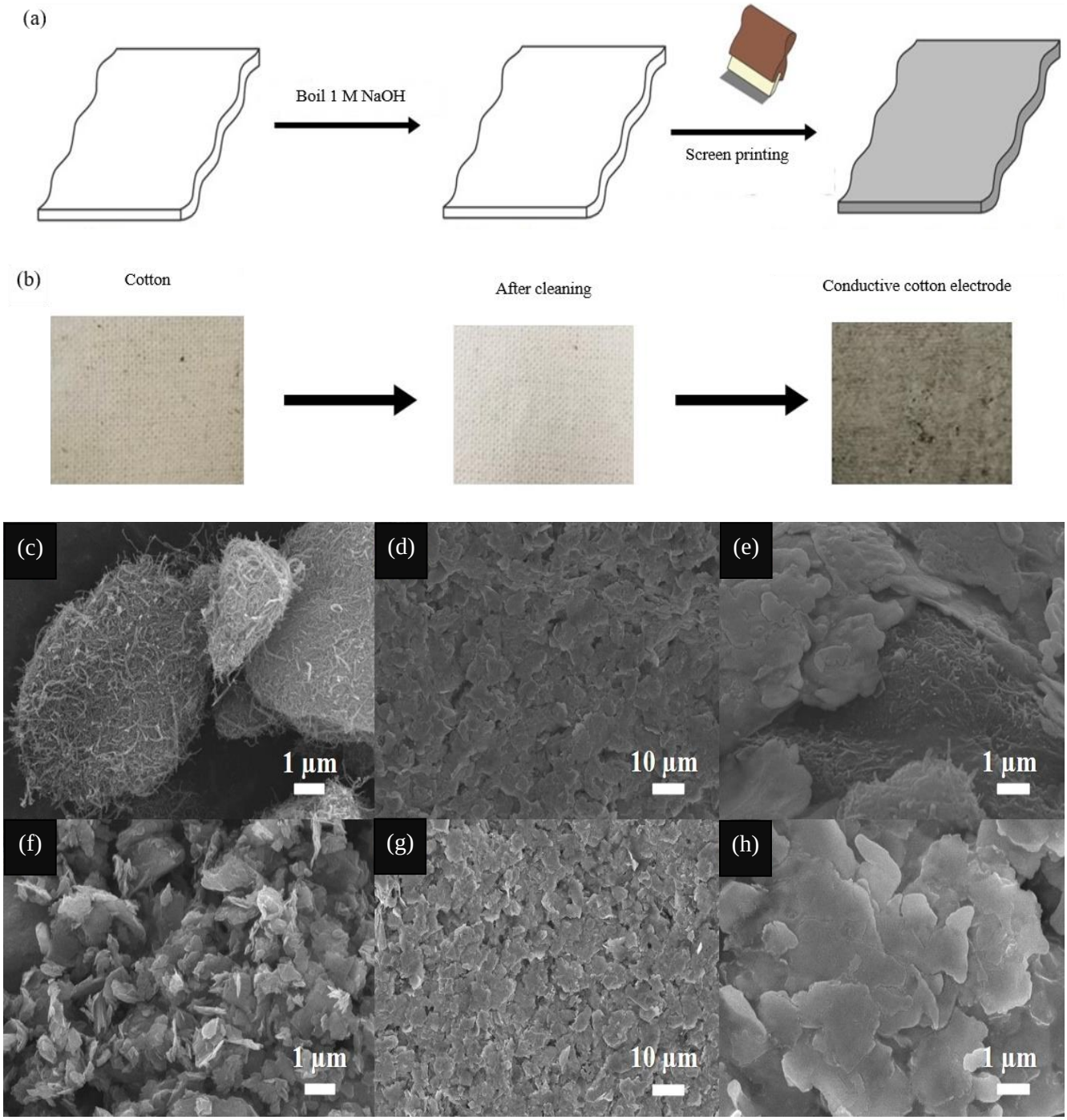

Figure 1. (a) Schematic illustration for the fabrication process of conductive cotton electrodes, (b) true-color optical images obtained for the process of conductive cotton textiles after cleaning, and coated with graphene or CNT; SEM images of (c) carbon nanotubes (CNTs), (d) conductive screen print cotton (CSPC) prepared with silver powder and textile ink, (e) CSPC prepared with CNTs, silver powder and textile ink, (f) graphene nanoflakes, (g) conductive coating of silver powder with textile ink and (h) CSPC prepared with graphene, silver powder and textile ink.

The CSCP electrodes were cut and designed for the assembly of a flexible supercapacitor device as shown in Figure 3(a). An optimized concentration of PVA-KOH solid gel electrolyte was used in this study according to our earlier investigations [22]. The areal specific capacitances obtained at different current densities of the device are shown in Figure 3(b). When the performance of the fabricated flexible device was investigated, the specific areal capacitance values of 677.12, 282.75, 298.89, 288.75 and 319.17 $mF \cdot cm^{-2}$ were obtained at the rate of 0.0125, 0.05, 0.0625, 0.125 and 0.1875 $mA \cdot cm^{-2}$, respectively. Moreover, the flexibility of the fabricated supercapacitor device was examined at different twisted bending angles using the cyclic voltammetry experiments. Figure 3(c) shows the cyclic voltammograms obtained after bending of the device at different angles of 30°, 45°, 60°, 90° and return to the flat position (0°). It should be noted that the shapes of all the CV curves recorded at various angles are almost similar in pattern and a slight variation in the area under the CV loop was observed due to severe stress caused by the extreme bending of the device which can affect the inner contact region of the interface between the electrode and electrolyte. The corresponding specific capacitance retention at 0°, 30°, 45°, 60°, 90° was found to be 100, 97.54, 92.54, 89.19 and 88.16%, respectively and retained the value of 99.62% once the bending was returned to 0° from 90° (Figure 3(d)), indicating excellent flexibility of the device was attained even at different twisting angles which fulfilling the major requirements for the mechanical deformation of the wearable electronics. Furthermore, the cyclic stability of the device was characterized using cyclic voltammetry at a fast scan rate of 100 $mV \cdot s^{-1}$ (Figure 3(e)), which showed outstanding cyclic stability (> 95%) for the first 1000 CV cycles followed by a slightly decreased tendency of the capacitance retention was observed and eventually the overall specific capacitance retention value was found to be ~80% for over 3,000 cycles. It could be observed that the shapes of the CV curves recorded at the initial and final cycles after long-term stability test (Figure 3(f)) displayed no significant changes indicating the extraordinary cyclic stability of the flexible devices using the conductive cotton electrodes. These results demonstrated that the fabricated symmetric flexible supercapacitor device assembled with the optimized electrode composition of the 6AC-CSPC specimens shows excellent specific capacitance retention and exceptional cyclic stability even after the device was twisted at different bending angles leading to its potential practical applications in portable electronics.

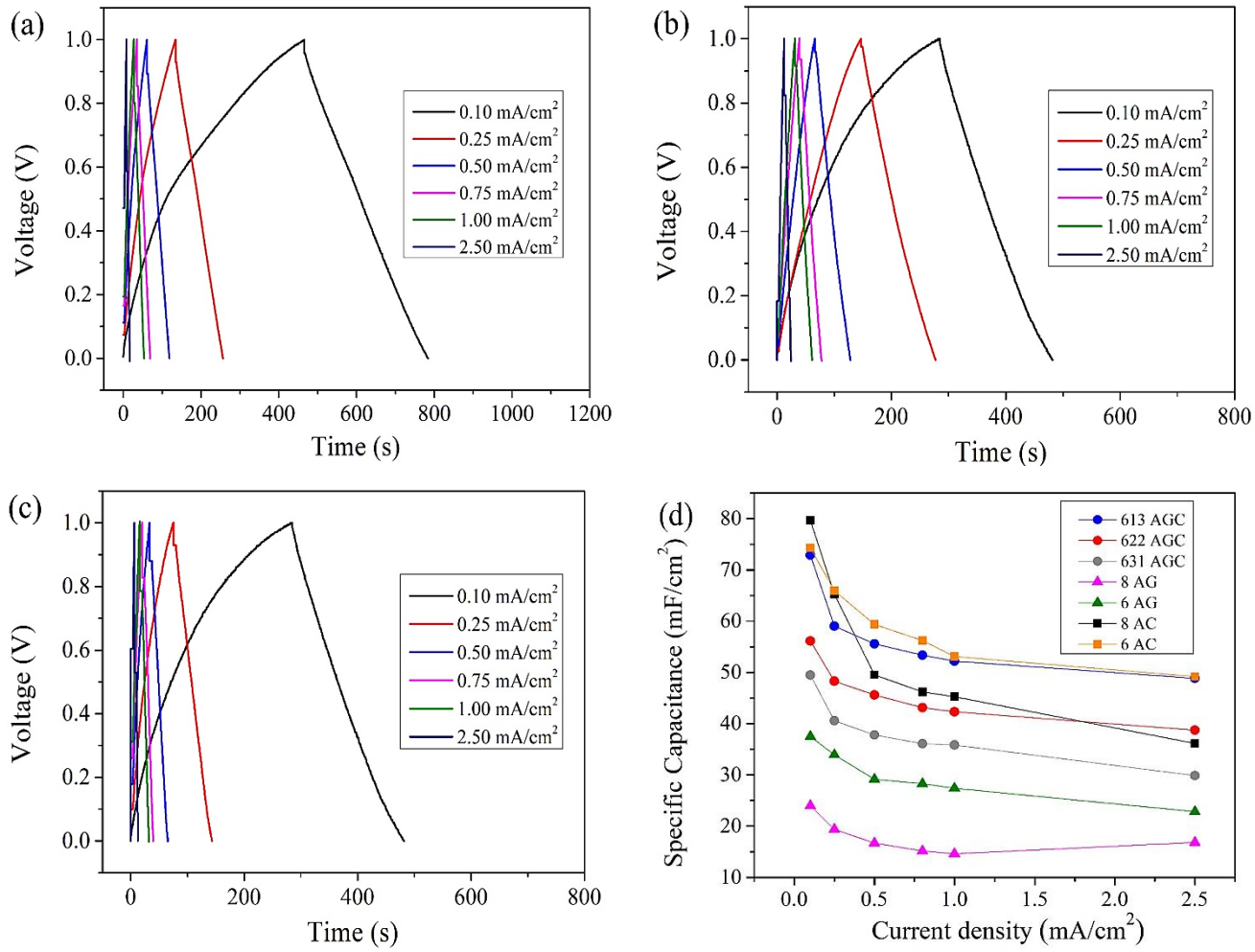

Figure. 2. The galvanostatic charge-discharge (GCD) profiles of various electrode composition obtained at different current densities for (a) 6AC (60% silver + 40% CNTs), (b) 6AG (60% silver + 40% graphene), (c) 613AGC (60% silver + 10% graphene + 30% CNTs) and (d) the plot of specific capacitance versus current density for the conductive cotton prepared with different ratio of CNTs and graphene.

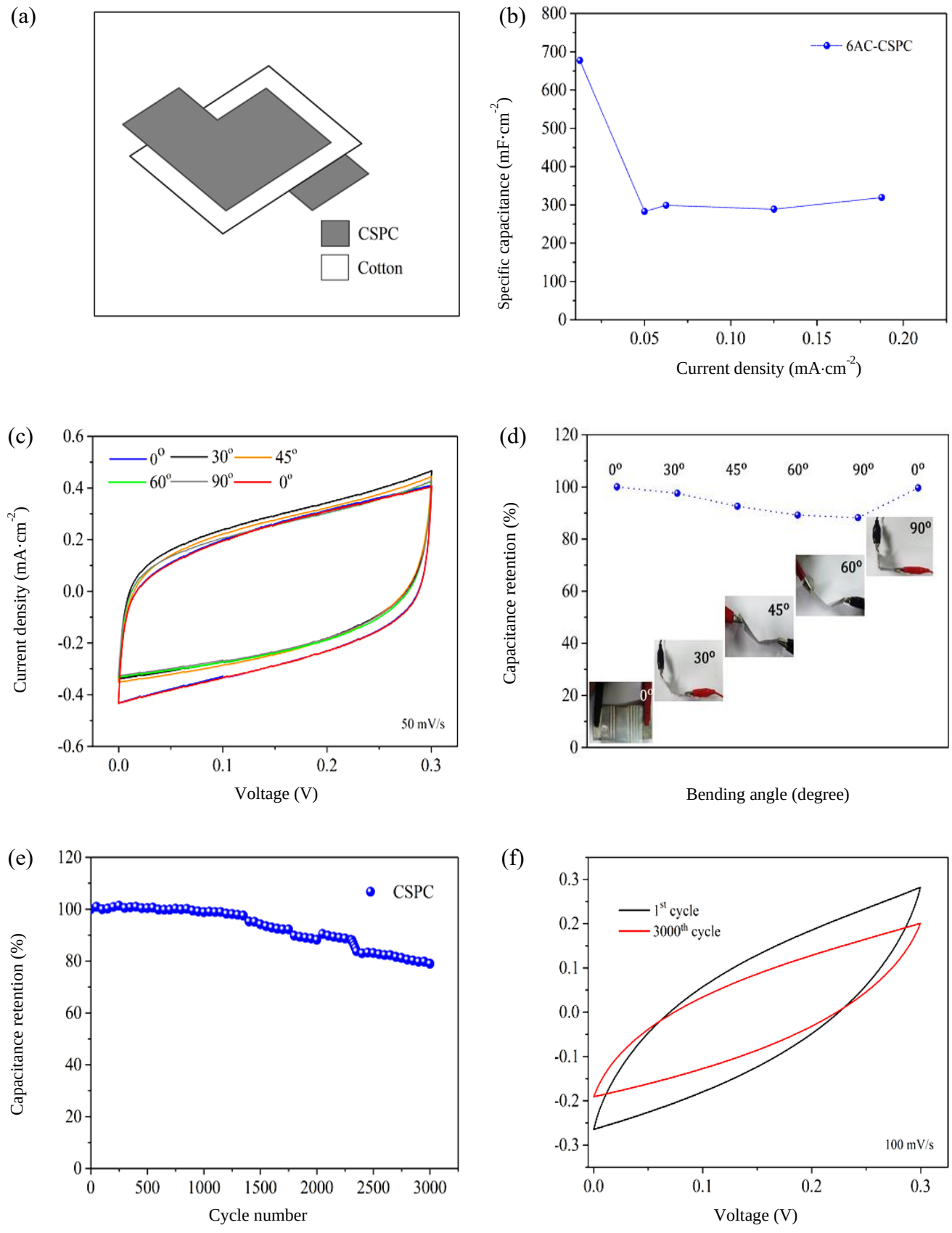

Figure 3. (a) Schematic diagram of the flexible supercapacitor assembly, (b) the specific areal capacitance of the flexible device fabricated using two symmetric electrodes (6AC-CSPC) obtained at different current density, (c) CVs of the flexible device recorded at different bending angles of 0°, 30°, 45°, 60°, 90° and recovered to 0°, (d) capacitance retention at different bending angles (inset images show the digital photographs taken at different bending angles), (e) cyclic stability of the flexible device for over 3000 CV cycles, and (f) CVs of the 1st and after 3000th cycle (100 mV·s $^{-1}$).

4. Conclusions

In summary, the conductive cotton-based textile electrodes were successfully fabricated using the coating ingredients of silver powder, textile ink and different carbon nanomaterials such as CNTs and graphene as the active components through the screen printing method. The electrodes prepared with the CNTs sources show an excellent electrical conductivity, improved electrochemical performance, better rate ability and stability in a strong alkaline electrolyte (6M KOH). Moreover, a symmetric solid-state flexible supercapacitor device was successfully fabricated with the high-performance electrodes using the PVA-KOH gel electrolyte system. The highest areal specific capacitance of 677.12 $mF \cdot cm^{-2}$ at 0.0125 $mA \cdot cm^{-2}$ was achieved for the device having suitable electrode composition of the 6AC-CSPC specimens (60% silver + 40% CNTs) which retains better flexibility under severe mechanical deformation of different bending angles and shows outstanding cyclic stability for over 3000 CV cycles. These results demonstrate that the high potential of CSPC textile electrodes can further be extended into advanced flexible energy storage devices for viable applications.

Acknowledgments

Authors acknowledge the financial support from TRF-IRN Program granted to the International Research Network on Electroplating Technology (IRN61W0002).

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