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# A flexible cable-shaped supercapacitor based on carbon fibers coated with graphene flakes for wearable electronic applications

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**Abstract**

This work presents a flexible cable-shaped supercapacitor based on carbon fibers (CFs) coated with graphene flakes (GFs) for wearable electronic applications. The CF bundles were adopted as base materials and the GFs were coated on the surface of CFs using a simple dipping method for the enhancement of the specific surface area and the higher conductivity of flexible electrodes. $H_2SO_4$ was mixed with poly(vinyl alcohol) (PVA) to form a gel electrolyte, which can prevent leakage. Polydimethylsiloxane (PDMS) was selected as a packaging material to fabricate the proposed flexible supercapacitor due to its flexibility and good thermal and chemical stability. From the electrochemical analysis, the fabricated device exhibited 15.099–6.492 mF/cm$^2$ of specific capacitance and 2.097–0.902 μWh/cm$^2$ of energy density in the range of 50–300 mV/s of scan rate. These values were about 1.9 times larger than the supercapacitor without being coated with the GFs. In addition, the specific capacitance showed small difference of 3.4% between straight and twisted positions, which assures the mechanical stability of the flexible cable-shaped supercapacitor.

**Keywords:** Flexible supercapacitor, Carbon fibers, Graphene flakes, Gel electrolyte, Wearable electronics

## Introduction

As wearable electronic devices become popular, there is an increasing demand for flexible energy storage devices which have a large output range and power density [1–2]. Furthermore, energy storage devices should be flexible, lightweight and compatible with wearable electronic devices. Therefore, various types of energy storage devices such as supercapacitors [3], solar cells [4], lithium-ion batteries [5] and thermoelectric generators [6] have been researched over the last decade. Among those developed devices, supercapacitors, also called electrochemical capacitors or ultracapacitors, have been considered as the most adequate alternative for wearable electronic applications through their attractive features such as long lifecycle and high power density [7]. In addition, they have several advantages like a wide temperature range and chemical stability, which are appropriate for the wearable purpose. For example, Some groups presented supercapacitors based on flexible substrate using photolithography process [8–11]. Meng et al. reported a polymer-based thin supercapacitor with carbon nanotube (CNT)/polyaniline (PANI) nanocomposite electrodes using an electropolymerization method [12]. Some other groups presented printed planar supercapacitor using different printing method [13–16]. However, in these works, the deposited electrode materials were exposed, which can easily be detached from their substrates and nonelastic substrates were applied, which limit their use in wearable electronic applications [17–18].

In this research, to meet the demands of flexibility, we applied a polydimethylsiloxane (PDMS) elastomer due to its simple fabrication process and low Young's modulus of 1.8 MPa, which also shows an elongation at a failure of 160%, a material with chemical and thermal stability. For example, Chen et al. fabricated a stretchable supercapacitor based on carbon nanotube sheets on the PDMS [19]. However, it showed a limitation for wearable electronic applications since the device was not fully packaged.

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Therefore, the exposed gel electrolyte can cause performance degradation and its acidic feature is not biocompatible to human skin. Also, it has the problem of mechanical stability under repeated deformations such as bending and stretching.

In this research, we successfully developed a flexible cable-shaped supercapacitor based on carbon fibers (CFs) coated with graphene flakes (GFs) for wearable electronic applications. For fabricating electrodes, CF bundles were adopted as base materials. For the enhancement of the specific surface area and conductivity of the electrodes, GFs were coated on the CFs using a dipping method. For the electrolyte, $H_2SO_4$ was mixed with poly(vinyl alcohol) (PVA) for the formation of the gel phase, which makes it free from leakage problem. Lastly, for packaging all these materials, PDMS was selected owing to its flexibility and good thermal and chemical stability, also maintains the proposed supercapacitor's electrochemical properties under mechanical deformation.

## Design and fabrication

The proposed flexible cable-shaped supercapacitor consists of electrodes, gel electrolyte, and PDMS elastomer, which was used for packaging the device as shown in Fig. 1. For the electrodes, CFs (7 μm diameter, TORAYCA®, Toray Industries, Inc., Japan) were selected as base materials. These CFs have good electrical and mechanical properties with long shape, which is appropriate for the cable-shaped supercapacitor [20]. For the increment of specific surface area and electric properties of the electrodes, GFs were deposited on the surface of fiber bundle by dip-coating into graphene dispersion (7 nm average thickness, Graphene Supermarket, U.S.A.) diluted with *n*-butyl acetate (Supelco Inc., U.S.A.). For the electrolyte, $H_2SO_4$ (ACS reagent, 95.0–98.0%, Sigma-Aldrich, U.S.A.) was selected because of its high capacitance among other materials which were used for supercapacitors in previous research [21]. Thus, in order to form a gel phase, PVA ($M_w$ 89,000–98,000, 99+ % hydrolyzed, Sigma-Aldrich, U.S.A.) was mixed and heated with $H_2SO_4$. Finally, PDMS (Sylgard® 184, Dow Corning) was selected as the packaging material due to its novel chemical and thermal stability [22].

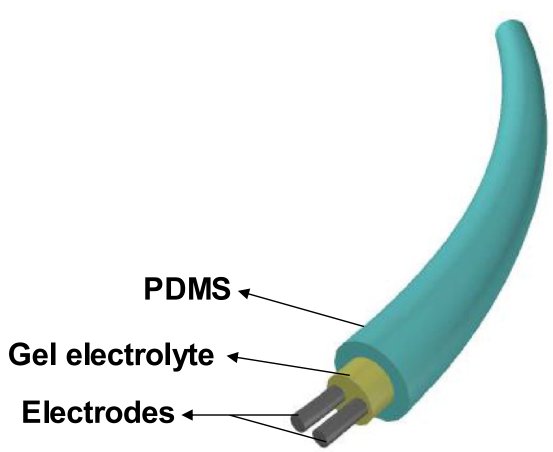

**Fig. 1** Schematic diagram of the proposed flexible cable-shaped supercapacitor

The schematic diagram of fabrication sequences is shown in Fig. 2. First, two bundles of 20 cm CFs were dip-coated in the 7 wt% of graphene dispersion diluted with *n*-butyl acetate (Sigma-Aldrich, U.S.A.) and heated at 250 °C for 150 min to evaporate the solvent. GFs-coated CF bundles were then twisted with a wire rotator (Lab Mart, South Korea) 20 times in order to form each electrode. Gel electrolyte was fabricated in the following steps: 100 mL deionized (DI) water, 10 mL $H_2SO_4$ (ACS reagent, 95.0–98.0%, Sigma-Aldrich, U.S.A.) and 10 g PVA were stirred and heated on a hot plate stirrer at 180 °C and 600 rpm for 40 min. The electrolyte solution became transparent after 20 min and turned into a gel phase when the solution temperature reached 70 °C. After disposing of a pair of CF bundles, the pre-made gel electrolyte was coated and dried at room temperature for 24 h. To make a cable shaped device, a commercial silicone shrinkable tube was employed as a mold for the packaging material, PDMS. Before placing the CF bundles, the release agent was sprayed inside the tube for easy removal of the tube after curing the PDMS. After placing the bundles into the tube, PDMS solution mixed the base and curing agent at the ratio of 20:1 was injected using a syringe. To prevent changing the electrolyte properties, the PDMS was cured at room temperature for 48 h and the tube was finally detached from the PDMS. The proposed flexible cable-shaped supercapacitor was successfully fabricated with 20 cm in length and 4 mm in thickness. For the electrochemical measurements, commercial copper wires were connected to both ends of the electrodes of supercapacitor with Ag paste.

## Experimental results and discussion

Figure 3a shows a photograph of the fabricated flexible cable-shaped supercapacitor. As mentioned in the design and fabrication section, the $H_2SO_4$/PVA gel electrolyte-coated CFs/GFs electrodes were surrounded by PDMS providing highly flexible structure. The fabricated supercapacitor could be changed into various states like freely bent-state (Fig. 3b) and twisted-state (Fig. 3c) and with its high flexibility. It was found that the electrodes and the electrolyte were fully embedded into the PDMS in stable position.

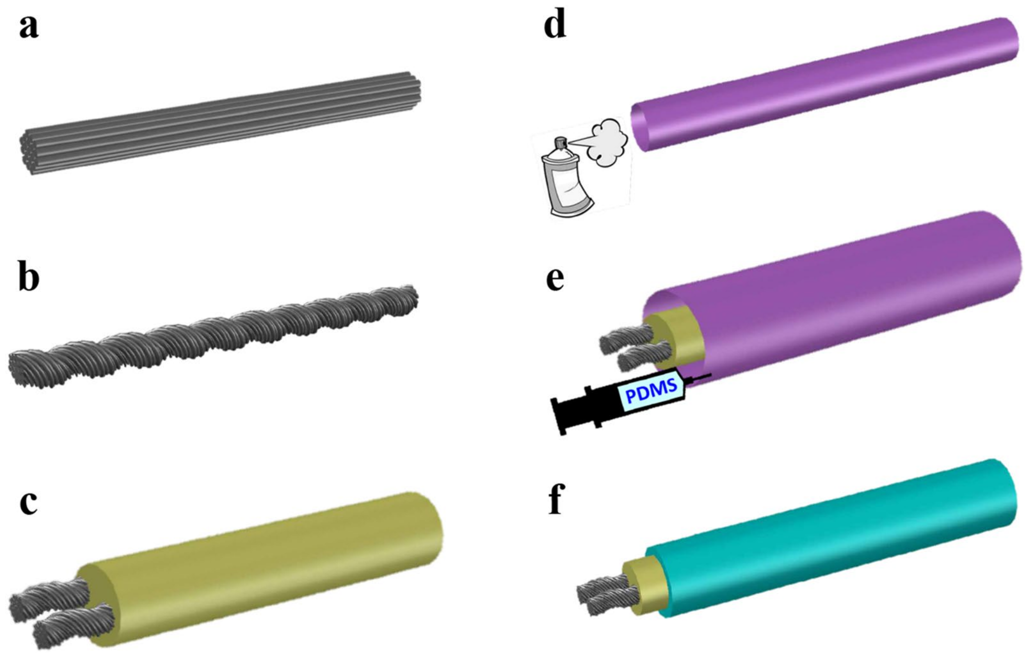


**Fig. 2** Fabrication sequences of the proposed flexible cable-shaped supercapacitor: **a** deposition of GFs on the surface of the CF bundles, **b** 20 times twisted CF bundles, **c** deposition of gel electrolyte, **d** spraying of release agent, **e** injection of PDMS, and **f** removal of the shrinkable tube

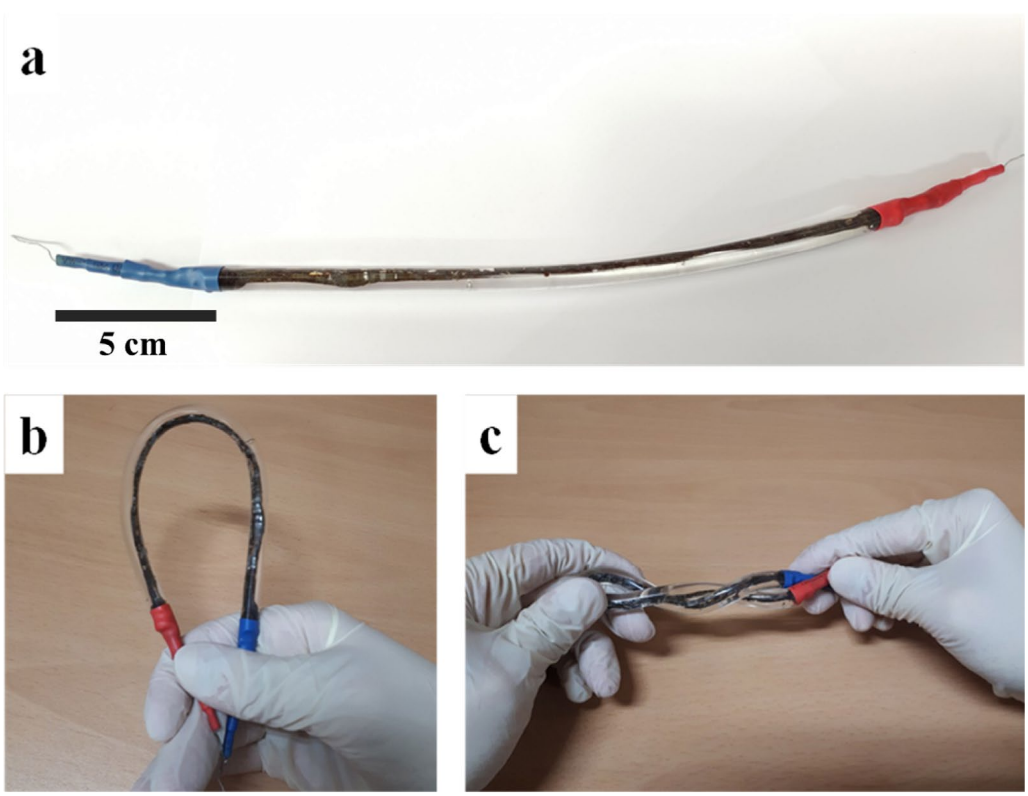


**Fig. 3** Photographs of the fabricated flexible cable-shaped supercapacitor: **a** normal state, **b** bent-state, and **c** twisted-state

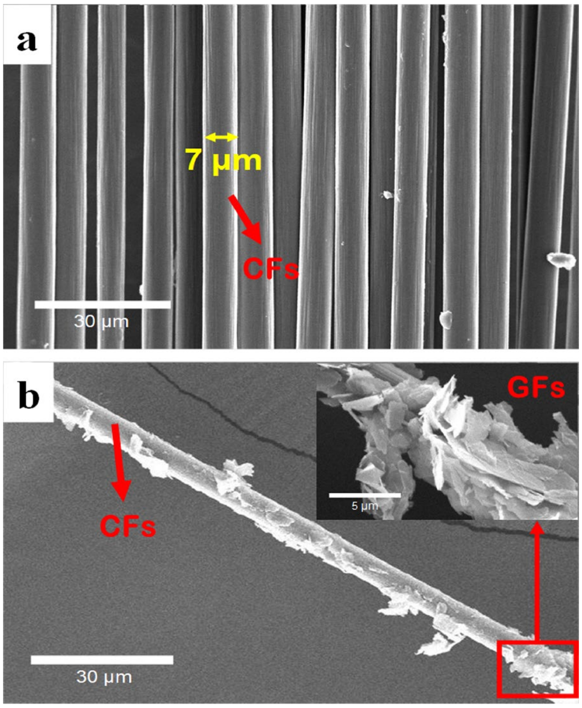


**Fig. 4** FE-SEM images: **a** before and **b** after being coated with GFs on the surface of CFs

The surface morphologies of the bare and GFs-coated CFs were analyzed using a field emission scanning electron microscopy (FE-SEM) (S-4800, Hitachi High-Technologies Co., Ltd.) operating at 10 kV. It can be observed that the bare CFs show clear and planar surface as shown in Fig. 4a. However, after the deposition of GFs, the rougher surface as shown in Fig. 4b was observed, which attributes to higher active surface area and specific capacitance.

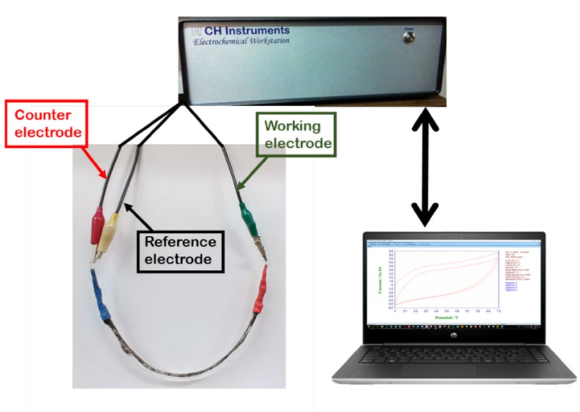


**Fig. 5** Test setup for the electrochemical analysis of the fabricated supercapacitor

Finally, for the electrochemical characterization of the fabricated flexible supercapacitor, cyclic voltammetry (CV) and galvanostatic charging–discharging (GCD) measurements were performed using an electrochemical workstation (660E, CH Instruments, U.S.A.) in straight and twisted states. Test setup was depicted in Fig. 5. The CV curves measured in a potential range from 0 to 1 V at

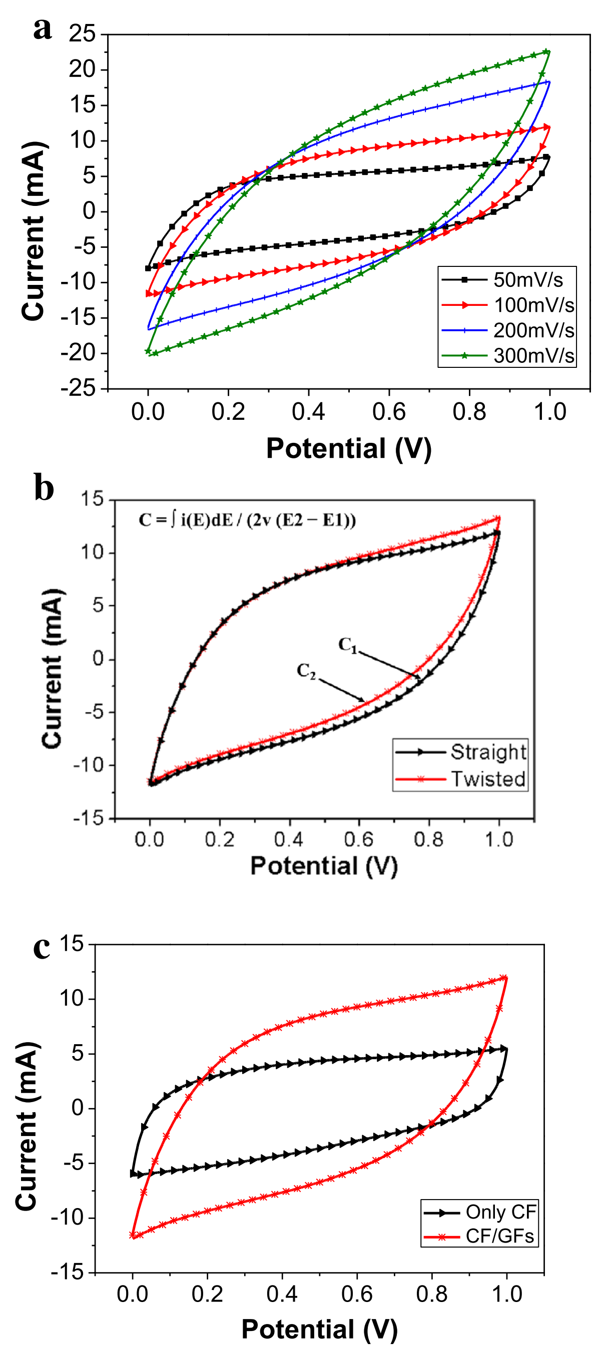


**Fig. 6** Cyclic voltammetry (CV) curves: **a** under various scan rates, comparison between **b** straight and twisted position, and **c** before and after being coated with GFs at the scan rate of 100 mV/s

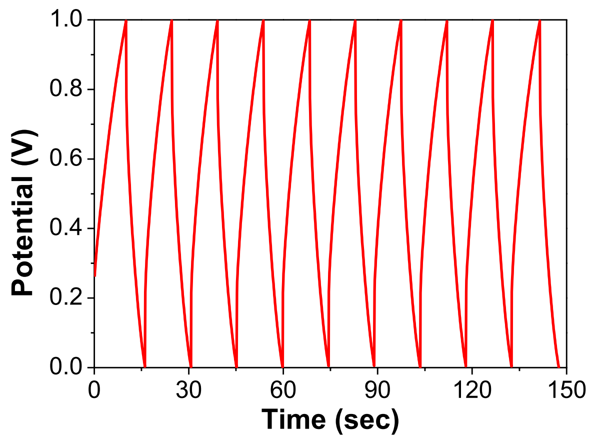


**Fig. 7** Galvanostatic charging–discharging (GCD) curve under current of 10 mA

various scan rates from 50 to 300 mV/s were presented in Fig. 6a. It can be observed that the CV curves show a rectangular shape, which means that the cable-shaped supercapacitor shows an electric double-layer capacitor (EDLC) behaviors. The comparison between CV curves at the straight and twisted position was shown in Fig. 6b, which showed 3.4% of small difference in specific capacitance (calculated form mentioned equation in the figure). Figure 6c indicates the comparison between before and after the coating of GFs on the CF surface. After the GFs coating, the integrated area of the CV curve was about 1.9 times larger than that of before coating, this value is proportional to specific capacitance and energy density. In addition, the comparison between CV curves at the normal and under stress position was shown in Fig. 6b. It indicated that performances of our fabricated

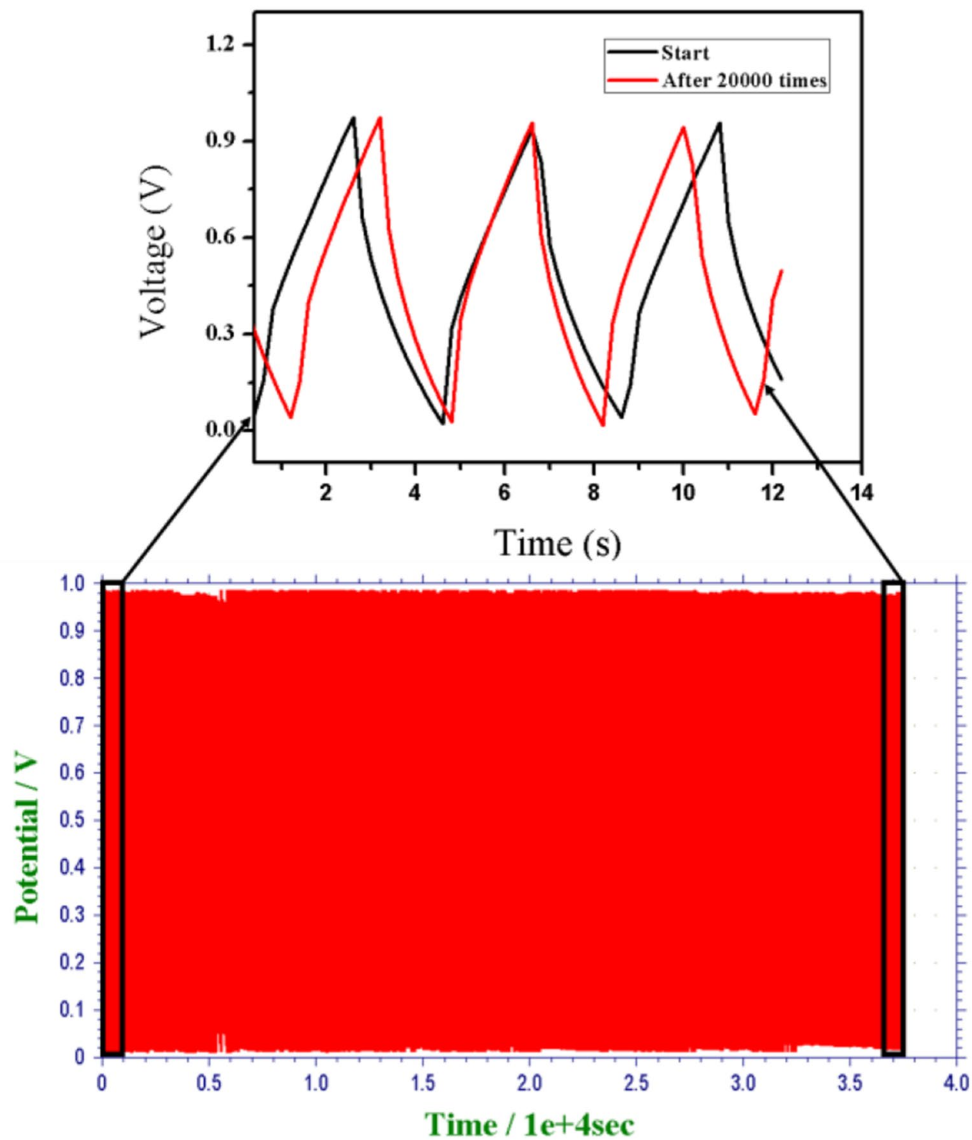


**Fig. 8** Galvanostatic charging–discharging curves and its cycle life (20,000 segments)

**Table 1 Comparison of the capacitance, energy density of our supercapacitor with other works**

| Electrode material | Preparation method | Substrate | Electrolyte | $C_A$ (mF $cm^{-2}$) | $E_A$ (μWh $cm^{-2}$) | References |
|---|---|---|---|---|---|---|
| rGO | Photolithography and in-situ assembled graphene | PET | PVA-$H_2SO_4$ | 0.95 | – | [23] |
| LSG | Laser-scribed graphene | Flexible substrate | PVA-$H_2SO_4$ | 2.32 | 0.32 | [24] |
| EG/PH1000 | Spray coating | Paper/PET | PVA-$H_2SO_4$ | 5.4 | – | [25] |
| GFs-CFs | GFs coating | PDMS | PVA-$H_2SO_4$ | 15.099 | 2.097 | This work |

supercapacitor will not change much even under different situations. At last, the GCD measurement was analyzed and shown in Figs. 7 and 8. they showed quite uniform charging and discharging time to indicate the good energy storage performance and good life cycle of the fabricated cable-shaped supercapacitor. From CV and GCD measurements, 15.099–6.492 mF/$cm^2$ of specific capacitance and 2.097–0.902 μWh/$cm^2$ of energy density were obtained in the range of 50–300 mV/s of scan rate, respectively. The comparison between our fabricated supercapacitor and other works was shown in Table 1 and it shows good performances in the wearable supercapacitor devices.

## Conclusions

In summary, this research reports a flexible cable-shaped supercapacitor based on CFs coated with GFs for wearable electronic applications. The graphene-coated flakes on the surface of CFs much improved the electrodes' specific surface area and electrical conductivity, which leads to higher specific capacitance. From the electrochemical analysis, the obtained rectangular shape of the CV curves showed the ideal EDLC property of the flexible cable-shaped supercapacitor. The high specific capacitance of 15.099–6.492 mF/$cm^2$ and energy density of 2.097–0.902 μWh/$cm^2$ were obtained in the range of 50–300 mV/s of scan rate, respectively. These values were about 1.9 times larger than the supercapacitor without being coated with GFs on the surface of CFs. Also, the specific capacitance just showed 3.4% of difference between straight and twisted position, which assures the mechanical stability of the fabricated flexible cable-shaped supercapacitor.

**Authors' contributions**

JK designed fabrication and experiments, and prepared the manuscript of this study. JY and XX participated in the analysis of this study. JYP conceived of the study, and participated in its design and coordination and helped to draft the manuscript. All authors read and approved the final manuscript.

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Not applicable.

**Competing interests**

The authors declare that they have no competing interests.

**Availability of data and materials**

All data generated or analysed during this study are included in this published article.

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## Publisher's Note



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