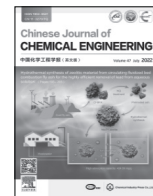




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Full Length Article

Chemical reduction-induced fabrication of graphene hybrid fibers for energy-dense wire-shaped supercapacitors

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ABSTRACT

The emerging one-dimensional wire-shaped supercapacitors (SCs) with structural advantages of low mass/volume structural advantages hold great interests in wearable electronic engineering. Although graphene fiber (GF) has full of vigor and tremendous potentiality as promising linear electrode for wire-shaped SCs, simultaneously achieving its facile fabrication process and satisfactory electrochemical performance still remains challenging to date. Herein, two novel types of graphene hybrid fibers, namely ferrocene oxide dots (FODs)@GF and N-doped carbon polyhedrons (NCPs)@GF, have been proposed *via* a simple and efficient chemical reduction-induced fabrication. Synergistically coupling the electroactive units (FODs and NCPs) with conductive graphene nanosheets endows the fiber-shaped architecture with boosted electrochemical activity, high flexibility and structural integrity. The resultant FODs@GF and NCPs@GF hybrid fibers as linear electrodes both exhibit excellent electrochemical behaviors, including large volumetric specific capacitance, good rate capability, as well as favorable electrochemical kinetics in ionic liquid electrolyte. Based on such two linear electrodes and ionogel electrolyte, a high-performance wire-shaped SC is effectively assembled with ultrahigh volumetric energy density (26.9 mW·h·cm⁻³), volumetric power density (4900 mW·cm⁻³) and strong durability over 10,000 cycles under straight/bending states. Furthermore, the assembled wire-shaped SC with excellent flexibility and weavability acts as efficient energy storage device for the application in wearable electronics.

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1. Introduction

Wearable electronics, especially intelligent fabrics, electronic skins, and implantable sensors, have recently become very popular [1–3]. However, these attractive wearable electronics require flexible energy storage devices as power sources. Wire-shaped supercapacitors (SCs) have emerged as ideal candidates for this purpose because of their intriguing features, including fast charging-discharging rates, high power characteristics, long-term durability and safe operating conditions [4–6]. More importantly, owing to their structural advantage, wire-shaped SCs may be more favorable for the construction of wearable electronics than conventional film- and bulk-type SCs directly utilized as fabrics in textile electronics [6–9]. Although some progress has been made, there still exist some issues in the development of wire-shaped SCs, especially the low volumetric energy density (<10 mW·h·cm⁻³) and the imbalanced problem between the device flexibility and electro-

chemical properties [10,11]. Typically, the wire-shaped SCs consists of two intertwined one-dimensional linear electrodes which are solidified in the solid-state gel electrolyte. Therefore, a suitable fiber electrode must be developed to build high-performance wire-shaped SCs in wearable electronics.

Compared with the rigidity of metal wire electrodes and the low conductivity of polymer fiber electrodes, carbonaceous fiber-based linear electrodes show great promise for wire-shaped SCs owing to their inherent advantages of light weight, small volume, and great conductivity [12–15], which could be integrated into textiles or wearable devices and provide maximum flexibility and wearability. Among them, graphene fiber (GF) holds great superiority to construct the wire-shaped SCs, which possesses the common characteristics of carbonaceous fibers like mechanical flexibility for textiles, as well as many outstanding advantages, such as tunable structure, excellent electrical conductivity and easy functionalization [16–20]. GF-based linear electrodes for wire-shaped SCs have been extensively researched through structural optimization or integration with other electroactive units [21–25]. Unfortunately, the practical application of GF-based linear

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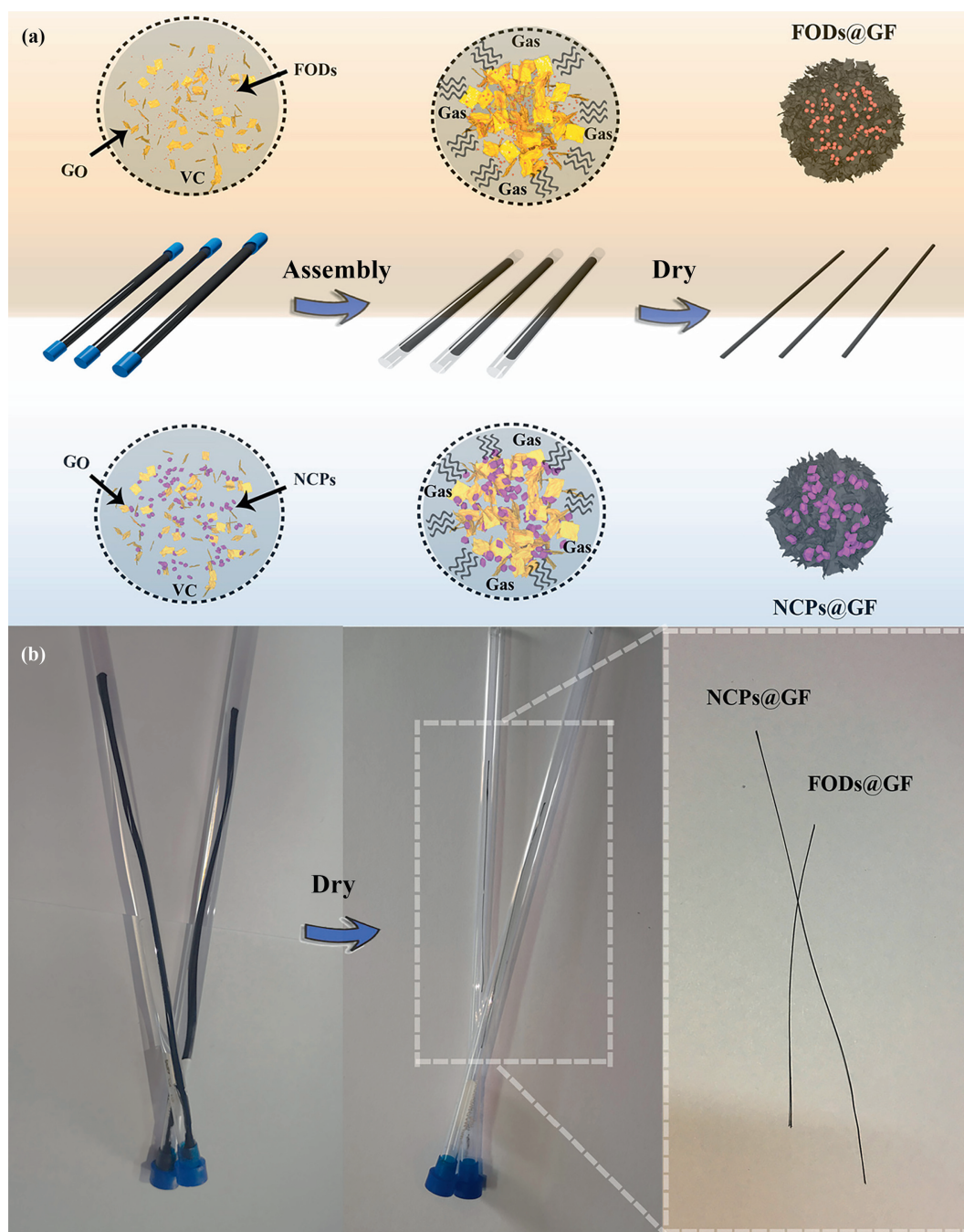


Fig. 1. (a) Schematic illustration and (b) digital photos of the chemical reduction-induced fabrication of FODs@GF and NCPs@GF hybrid fibers.

electrodes is still limited because of the low specific capacitance, sluggish electron transfer, and complicated fabrication. Therefore, the deep exploration of GF-based linear electrode with enhanced electrochemical behaviors is an urgent need for high-performance wire-shaped SCs.

Herein, we have successfully prepared two novel types of flexible GF-based linear electrodes, namely ferroferric oxide dots (FODs)@GF and N-doped carbon polyhedrons (NCPs)@GF, via an efficient chemical reduction-induced fabrication. When compared with common strategies such as the hydrothermal method, chemical vapor deposition method, and wet spinning method, the experimental conditions of the chemical reduction-induced fabrication are simple and mild, especially low reaction temperature

($\sim 80^\circ\text{C}$) and uncomplicated equipment. As a result, the chemical reduction-induced fabrication of the flexible GF-based linear electrodes is low cost and easy to be scaled up at an industrial level. Both FODs and NCPs as electroactive units are uniformly dispersed in graphene nanosheets to construct fiber-shaped architecture with high capacitive characteristics in an ionic liquid (IL) electrolyte, wherein conductive graphene nanosheets provide high connectivity for rapid electron transfer in FODs@GF and NCPs@GF linear electrodes. For real-life applications, a wire-shaped SC was effectively assembled based on ionogel electrolyte in which FODs@GF and NCPs@GF act as negative and positive electrodes, respectively. The fabricated device exhibits excellent flexibility and weavability, ultrahigh energy density ($26.9\text{ mW}\cdot\text{h}\cdot\text{cm}^{-3}$), and

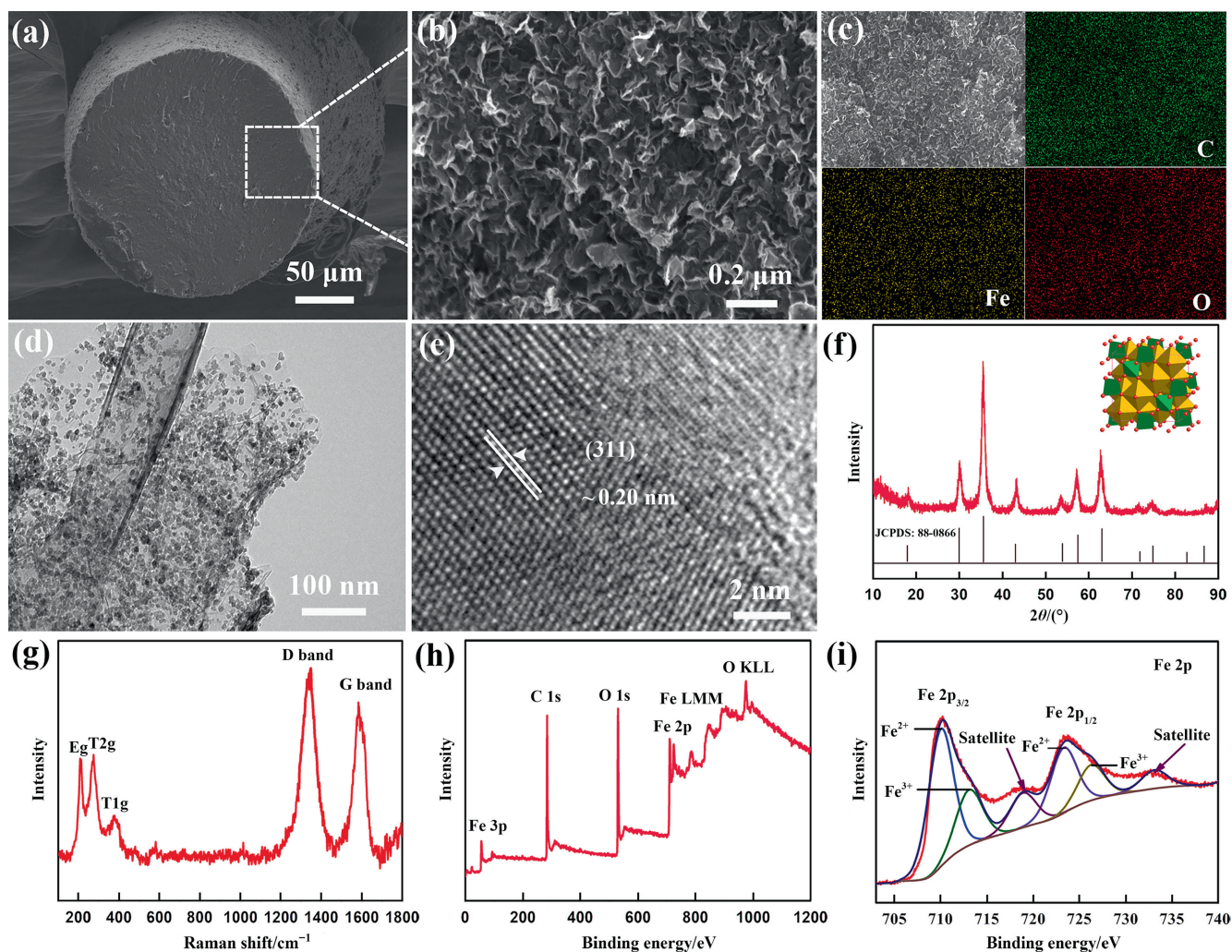


Fig. 2. SEM images with the (a) low and (b) high magnifications, (c) energy-dispersive spectroscopy (EDS) mapping images, (d) a typical TEM image, (e) corresponding high-resolution TEM (HRTEM) image, (f) XRD pattern, (g) Raman spectra, (h) XPS overall spectrum and (i) high-resolution Fe 2p spectra of the FODs@GF hybrid fiber.

strong durability ($\sim 83.7\%$ retention over 10,000 cycles), evidencing their great potential for application in portable/wearable electronics.

2. Experimental

2.1. Fabrication of FODs@GF and NCPs@GF

The FODs were synthesized *via* a chemical coprecipitation method previously reported (Fig. S1 in Supplementary Material). The NCPs were derived from a zeolitic imidazole metal-organic framework (Fig. S2). Typically, graphene oxide (GO) aqueous solution and an FOD dispersion were mixed under ultrasonication for 30 min, in which the mass ratio of FODs and GO was about 80:20. Under stirring, 50 mg of ascorbic acid (VC) was sequentially added into 20 ml of the uniform dispersion ($\sim 4 \text{ mg}\cdot\text{ml}^{-1}$). The mixed solution was then injected into several 5-mm-diameter tubes and sealed at both ends. After reacting at 85°C for 3 h, the glass tubes were unsealed and air-dried at 50°C to obtain FODs@GF, which was further heated to 200°C for 2 h in an inert atmosphere to remove residual VC. A similar method was employed for the preparation of NCPs@GF with a mass ratio of NCPs to GO of about 40:20 during the process.

2.2. Assembly of the wire-shaped SC

For assembling the wire-shaped SC, the FODs@GF and NCPs@GF were utilized as negative and positive linear electrodes, respectively. Additionally, ionogel electrolyte was effectively synthesized by mixing 0.8 g poly(vinylidene fluoride-hexafluoropropylene), 1.6 g 1-ethyl-3-methylimidazolium tetrafluoroborate IL, 1.2 g propylene carbonate, with 6.5 ml of acetone solution. The FODs@GF negative and NCPs@GF positive linear electrodes were immersed in this solution for 10 min. After removal from the solution, the two linear electrodes were completely encapsulated in the ionogel electrolyte and then simply intertwined with each other. The two twined linear electrodes were again thinly coated with ionogel electrolyte to firmly assemble the wire-shaped SC.

2.3. Material characterization

The morphology and microstructure of the as-prepared hybrid fibers were characterized by means of Hitachi SU8010 scanning electron microscope (SEM) and JEOL 2100F Transmission electron microscope (TEM). Chemical compositions were analyzed using X-ray diffraction (XRD; D8 ADVANCE), X-ray photoelectron spectroscopy (XPS; ESCLAB), and Renishaw high-resolution Raman

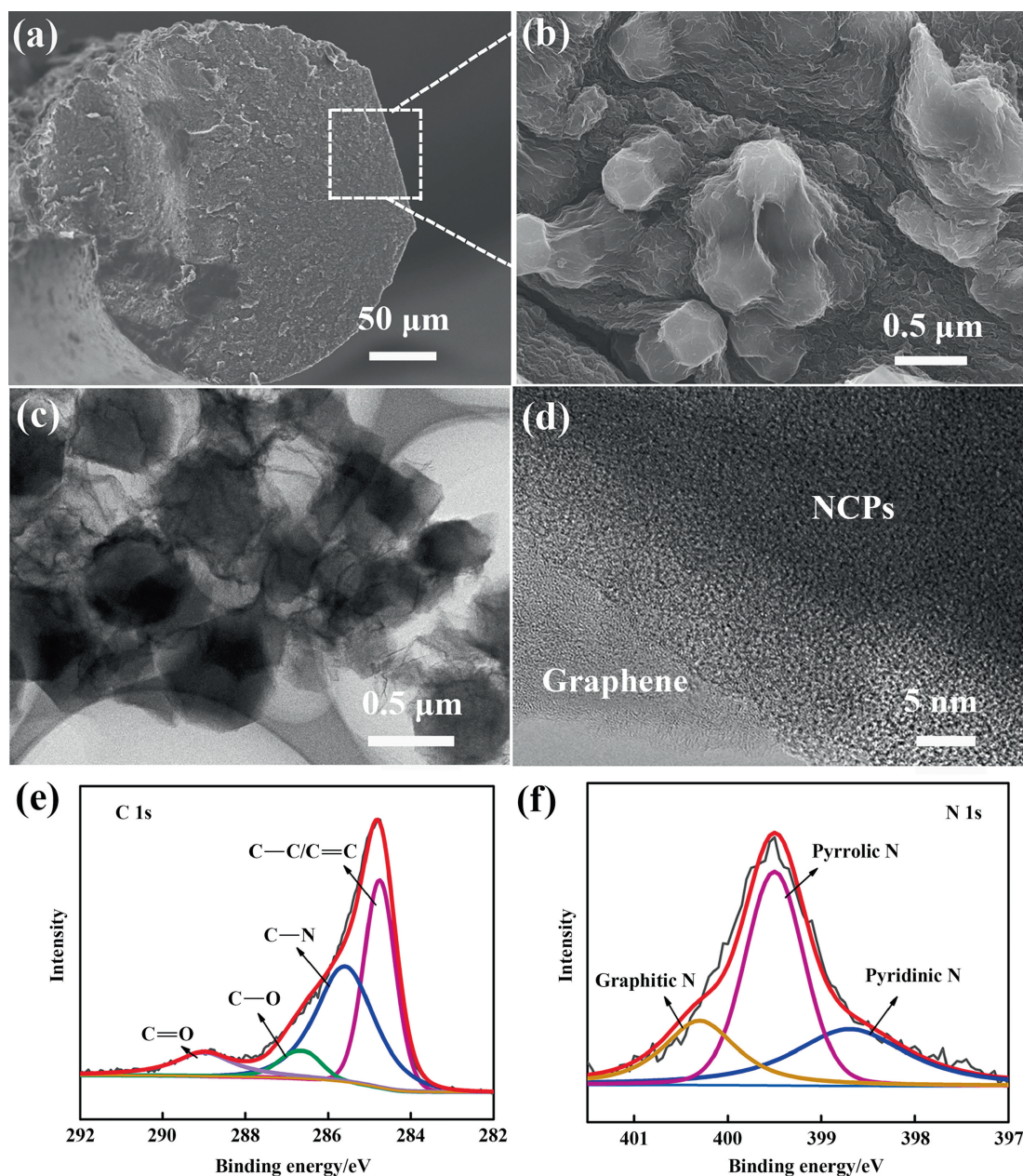


Fig. 3. SEM images at the (a) low and (b) high magnifications, (c) a typical TEM image, (d) the corresponding HRTEM image, (e) C 1s and (f) N 1s XPS spectra of NCPs@GF hybrid fiber.

spectra. All electrochemical tests were performed on an electrochemical station (VMP-300, Bio-Logic) at room temperature via common cyclic voltammetry (CV), galvanostatic charge–discharge (GCD), and electrochemical impedance spectroscopy over a frequency range of 0.01–100 kHz (EIS, 5 mV AC amplitude). Calculation methods of the volumetric specific capacitances of FODs@GF and NCPs@GF linear electrode, as well as the volumetric energy/power densities of the wire-shaped SC are provided in Supplementary Material in detail.

3. Results and Discussion

The preparation procedure of the FODs@GF and NCPs@GF hybrid fibers based on chemical reduction-induced fabrication is schematically illustrated in Fig. 1(a). Initially, a mixed solution of VC, GO, and FODs or NCPs is slowly injected into a glass tube. After

sealing the two ends of the pipe, the reduction of GO proceeds in the tube under a constant temperature of 85 °C when the VC as a reducing agent. During the process, as shrinkage of the GO and the gas pressure originating from the reduction of the GO oxygen-containing groups in the void space, the GO and FODs or NCPs tend to be columnar in the center of the glass tube to achieve effective assembly with each other owing to a chemical reduction-induced effect [26,27]. It is noted that this chemical reduction-induced fabrication should be conducted in a closed reactor under a certain amount of pressure. If the two ends of the glass tube are not completely sealed, the resulting hybrid fiber could be easily scattered and fractured. Compared with the wet fibers, the dried FODs@GF and NCPs@GF both exhibit the obvious shrinkage in length and diameter after being dried in air because of the water loss (Fig. 1(b)). As shown in Fig. S3, both two hybrid fibers with superior wearability can be readily knitted into cotton fabric and exhibit all-around flexibility and bendability.

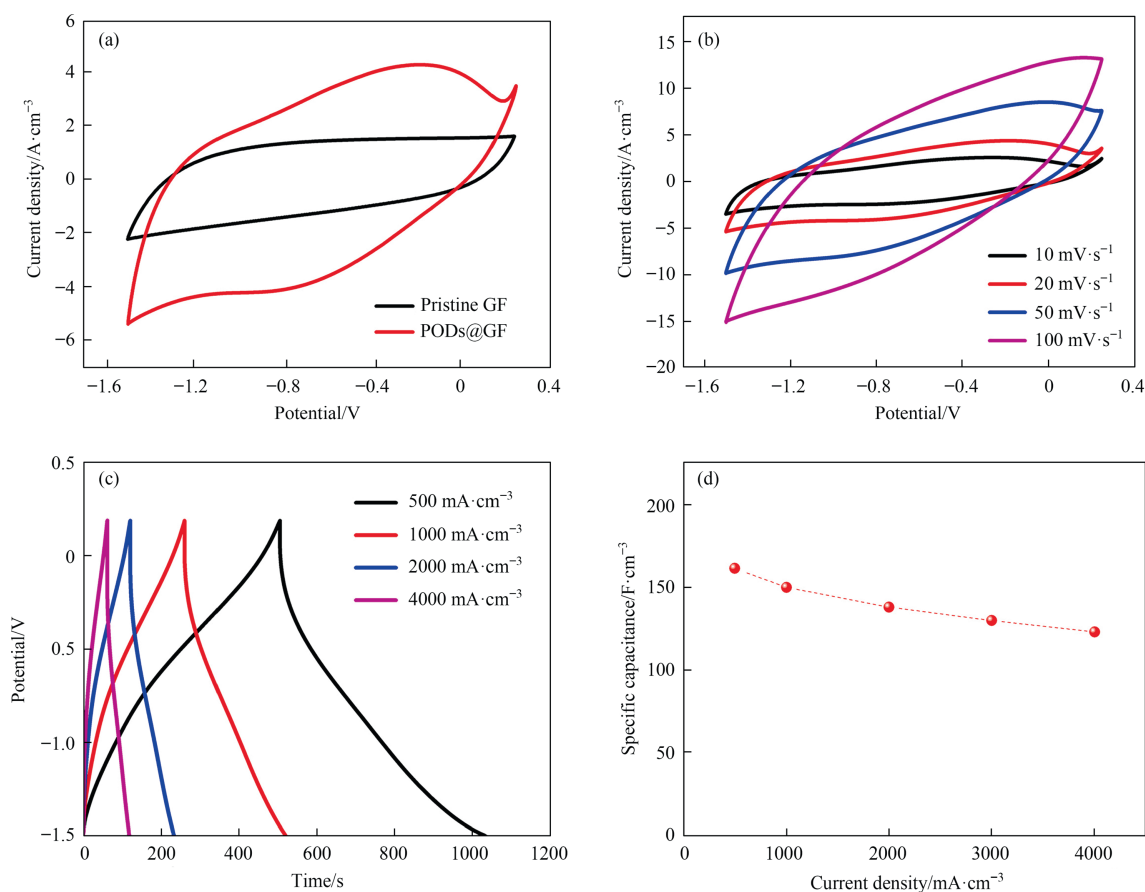


Fig. 4. (a) Comparative CV curves measured at the 20 mV·s⁻¹ of pristine GF and FODs@GF linear electrodes in IL electrolyte. (b) CV curves under various sweep rates and (c) GCD profiles at different current densities, (d) volumetric specific capacitances at different current densities of the FODs@GF linear electrode in IL electrolyte.

Fig. 2(a) shows a typical cross-sectional SEM image of the FODs@GF with a diameter of $\sim 200 \mu\text{m}$. Meanwhile, as observed from Fig. 2(b), the fiber surface is rough and densely wrinkled owing to the robust skeleton of the graphene nanosheets. Furthermore, the EDS mapping images indicate that the distribution of C, Fe, and O elements in the FODs@GF is uniform and constant (Fig. 2(c)), manifesting the successful dispersion of FODs in the graphene nanosheets. A TEM image (Fig. 2(d)) shows that numerous FODs with a uniform size of $\sim 10 \text{ nm}$ are anchored onto the graphene nanosheets without obvious aggregation. The well-defined lattice fringe of the FODs with a crystal interplanar spacing of $\sim 0.20 \text{ nm}$ is ascribed to the (311) plane of cubic spinel Fe_3O_4 (Fig. 2(e)). This phenomenon can be also evidenced by the XRD pattern (Fig. 2(f)) with the characteristic peaks attributed to the cubic spinel structural Fe_3O_4 (JCPDS no. 88-0866) [28].

The Raman spectra of the FODs@GF is presented in Fig. 2(g). Apart from D ($\sim 1350 \text{ cm}^{-1}$) and G ($\sim 1580 \text{ cm}^{-1}$) bands related to the graphene nanosheets, the major Raman bands are centered at $\sim 200\text{--}400 \text{ cm}^{-1}$ for the FODs@GF, which agreed well with the major vibrational features ($A_{1g} + E_g + T_{2g}$) of cubic spinel Fe_3O_4 [29,30]. In addition, the overall XPS spectrum (Fig. 2(e)) displays C, Fe, and O atoms without other impurities for the FODs@GF, whereas the high-resolution Fe 2p region could be divided into two spin-orbit doublets and two shakeup satellites, which is consistent with the Fe^{2+} and Fe^{3+} characteristic peaks of Fe_3O_4 [31,32], further indicating the effective formation of FODs (cubic spinel Fe_3O_4) in the FODs@GF hybrid fiber. High-resolution O 1s spectra of the FODs in the FODs@GF hybrid fiber before and after the process of VC reduction are shown in Fig. S4, which can be deconvoluted with three peaks of O_I , O_{II} , and O_{III} centered at 529.6, 531.1,

and 532.6 eV, corresponding to the oxygen present in the lattice, oxygen loss and absorbed oxygen on the surface, respectively [33–35]. Higher binding energy O_{II} peak around 531.1 eV is attributed to the oxygen vacancy, from which the values obtained for FODs before and after the process of VC reduction are 27.1% and 40.2%, respectively. Therefore, it can be revealed that the oxygen vacancy concentration of FODs is enhanced in the FODs@GF hybrid fiber after the process of VC reduction owing to the decrease of Fe valence.

Fig. 3(a) demonstrates that the obtained NCPs@GF exhibits a circular cross-section with a diameter of about $250 \mu\text{m}$. Within the hybrid fiber, numerous rhombic dodecahedral-shaped NCPs are homogeneously wrapped by graphene nanosheets, as confirmed by the SEM and TEM images (see Fig. 3(b) and (c)) of the NCPs@GF. Moreover, no obvious lattice fringe of NCPs can be observed in the HRTEM image (Fig. 3(d)), suggesting an amorphous NCP structure is decorated on the graphene nanosheets in the NCPs@GF. From the high-resolution C 1s spectra (Fig. 3(e)), two peaks at 286.6 and 288.4 eV, corresponding to C–O and C=O bonds [36,37], are relatively weak, indicating the effective reduction of GO oxygen-containing groups during the preparation of NCPs@GF. Furthermore, an obvious peak at 285.6 eV, attributed to the C–N bond [38,39], can be clearly observed, resulting from the abundant nitrogenous active sites of the NCPs in the hybrid fiber. From the results of the N 1s spectra shown in Fig. 3(f), there exists three binding energies located at 398.6, 399.4, and 400.7 eV, which are assigned to pyridinic N, pyrrolic N, and graphitic N [40,41]. As an outstanding electron donor, pyrrolic N offers high charge mobility, which considerably improves electron-transfer reactions [42]. Moreover, pyridinic N and pyrrolic N easily form rich additional

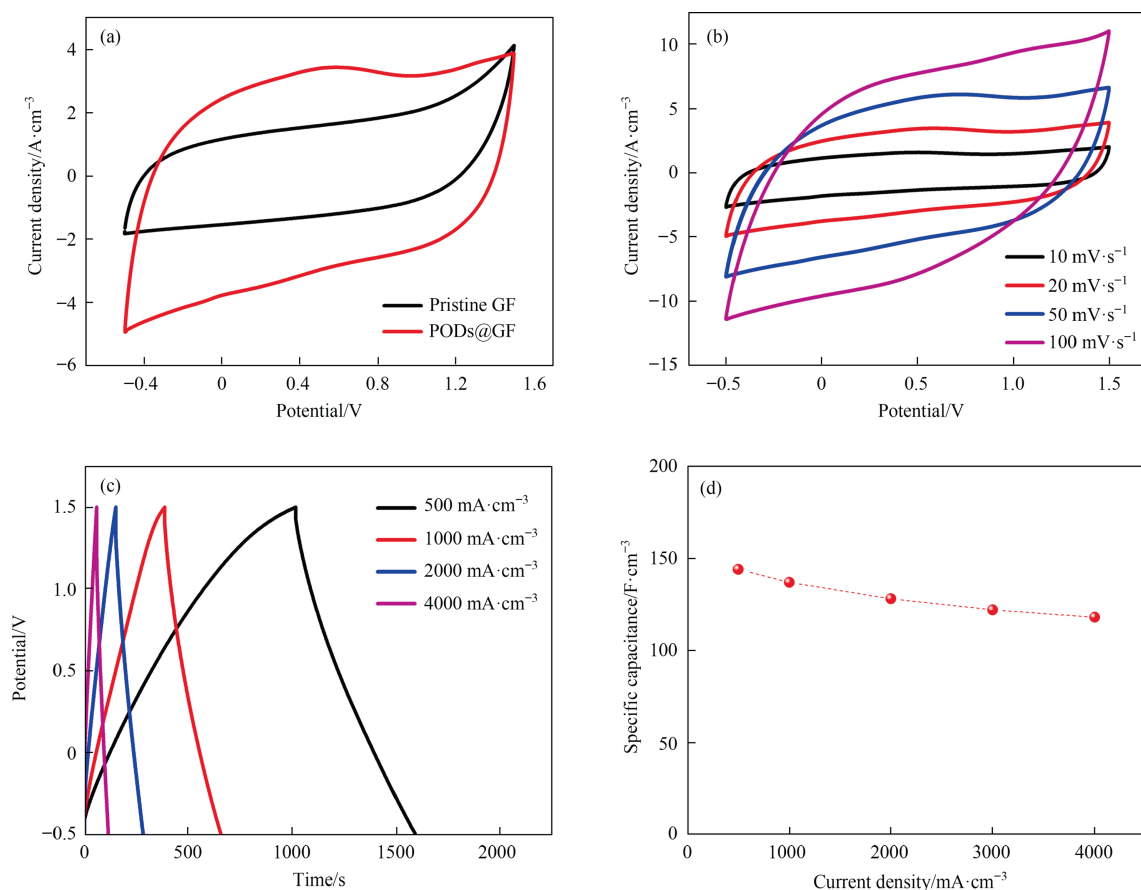


Fig. 5. (a) Comparative CV curves measured at the 20 mV·s⁻¹ of pristine GF and NCPs@GF linear electrodes in IL electrolyte. (b) CV curves under various sweep rates and (c) GCD profiles at different current densities, (d) volumetric specific capacitances at different current densities of the NCPs@GF linear electrode in IL electrolyte.

defects [42,43], providing more active sites for the rapid ionic kinetics of the NCPs@GF hybrid fiber.

The electrochemical behaviors of pristine GF and FODs@GF as the linear electrode were evaluated using a three-electrode configuration in IL electrolyte. As seen from Fig. 4(a), the CV curve of FODs@GF linear electrode exhibits a couple of broad redox peaks at -0.25 V (anodic peak) and -0.65 V (cathodic peak) within the negative potential range, delivering a larger specific capacitance than the pristine GF linear electrode with limited electric double-layer storage (rectangular-like CV curve). Furthermore, the set of redox peaks are obviously visible in various sweeping CV curves (Fig. 4(b)), while the GCD curves are nonlinear under various current densities (Fig. 4(c)), further revealing the existence of pseudocapacitive storage in the FODs@GF linear electrode during the electrochemical process. Due to the GF possessing only double-layer capacitance in IL electrolyte, it is concluded that the pseudocapacitive behaviors are associated with the redox reaction between IL ions and FODs in the FODs@GF linear electrode. To elucidate the evolution of FODs in the FODs@GF linear electrode during the electrochemical process, the chemical state variation of the Fe element was investigated through XPS analysis at the charging/discharging states (Fig. S5). The main peak of Fe 2p_{3/2} at 710.2 eV lightly shifts to a lower binding energy with deepening of discharge owing to the conversion of trivalent Fe to divalent Fe [44,45]. In turn, during the charging process, the valence state of the reduced divalent Fe can change to trivalent Fe, further indicating the reversible redox reaction of FODs in the FODs@GF linear electrode with IL ions to generate and store charge. In the previous research, it is reported that the [EMIM]⁺ cations as the working ions can trigger the pseudocapacitive reaction for Fe-based elec-

trodes [44–46]. Based on this, the pseudocapacitance of the FODs@GF linear electrode is mainly originating from the insertion/extraction of [EMIM]⁺ cations in the FODs, while [BF₄]⁻ anions are just adsorbed on the electrode surface. [EMIM]⁺ cations in a planar conformation can be inserted into the bulk of FODs in the FODs@GF linear electrode accompanied by the formation of divalent Fe during the discharge process, whereas [EMIM]⁺ cations are extracted during recharging. By calculation, the volumetric specific capacitance of the FODs@GF linear electrode reaches as high as 161.5 F·cm⁻³ in IL electrolyte at the current density of 500 mA·cm⁻³ (Fig. 4(d)), even higher than various GF-based linear electrodes previously reported in aqueous electrolytes, such as PPy@GF (107.2 F·cm⁻³) [47], MnO₂@GF (66.1 F·cm⁻³) [48], MoS₂@GF (30 F·cm⁻³) [49], and MWCNT@GF (25.9 F·cm⁻³) [50]. When the current density is increased to 4000 mA·cm⁻³, the volumetric specific capacitance still remains at a high value of 123.3 F·cm⁻³, indicating the remarkable rate capability of the resultant FODs@GF linear electrode in the IL electrolyte.

Fig. 5(a) presents the comparative CV curves of pristine GF and NCPs@GF as the linear electrode in IL electrolyte with potentials between -0.5 and 1.5 V. By contrast, the CV curve of NCPs@GF linear electrode not only possesses higher peak currents and a larger area, but also exhibits two small redox peaks owing to the surface redox reaction of nitrogenous active sites in NCPs@GF, thus revealing the superior capacitive storage of NCPs@GF linear electrode within the positive potential range. Additionally, the CV shape of the NCPs@GF linear electrode exhibits almost no distortion under various sweeping rates (Fig. 5(b)), indicating its excellent electrochemical kinetic characteristics in IL electrolyte. This can be also demonstrated by the GCD profiles (Fig. 5(c)) in the form of small

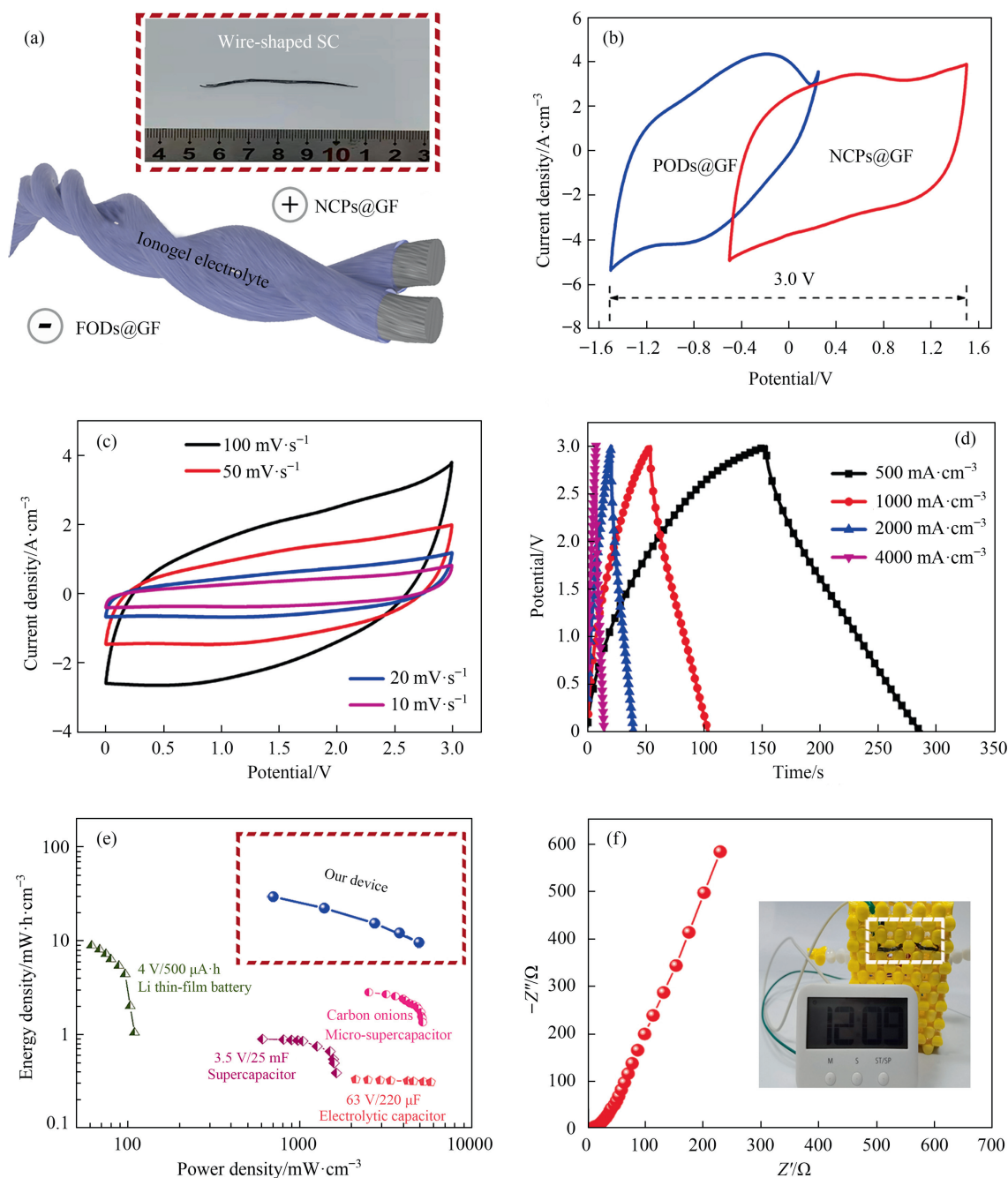


Fig. 6. (a) Schematic illustration and photograph of the wire-shaped SC based on FODs@GF and NCPs@GF linear electrodes. (b) Comparative CV curves of FODs@GF and NCPs@GF linear electrodes within different potential ranges according to the three-electrode configuration. (c) CV curves scanning at various rates (10–100 mV·s⁻¹). (d) GCD profiles under current densities (500–4000 mA·cm⁻³). (e) Ragone plot in comparison with the commercial energy storage devices, and (f) EIS plot of the assembled wire-shaped SC. (Inset (f) shows the energy storage performance of the wire-shaped SC as the wearable energy storage device).

“IR drop” within the discharge curves, evidencing the favorable capacitive behaviors of the NCPs@GF linear electrode. As a result, the NCPs@GF linear electrode shows remarkable rate capability (Fig. 5(d)) with large volumetric specific capacitances of 144.1, 137.4, 128.5 and 118.3 F·cm⁻³ under the current densities of 500, 1000, 2000, and 4000 mA·cm⁻³, respectively. Based on the above discussion, such flexible FODs@GF and NCPs@GF hybrid fibers as the linear electrodes both exhibit electrochemical behaviors in IL electrolyte, including large specific capacitance, excellent rate capability, as well as favorable electrochemical kinetics.

As a proof of concept, a novel wire-shaped SC has been assembled using ionogel electrolyte, for which the FODs@GF and

NCPs@GF serve as the negative and positive linear electrodes (Fig. 6(a)) due to their electrochemical capacitive-storage behaviors within the negative and positive potential ranges, respectively (Fig. 6(b)). Fig. 6(c) exhibits that the full set of CV curves without obvious distortion under various sweep rates ranging from 0 to 3.0 V, indicating the efficient ion/electron transportation of the assembled device with a high working voltage of 3.0 V. According to the GCD curves under different current densities (Fig. 6(d)), the volumetric energy/power densities of the wire-shaped SC were calculated, and their relationship was depicted using Ragone plots (Fig. 6(e)). The assembled wire-shaped SC delivers a large specific volumetric capacitance of about 33.8 F·cm⁻³, while the maximum

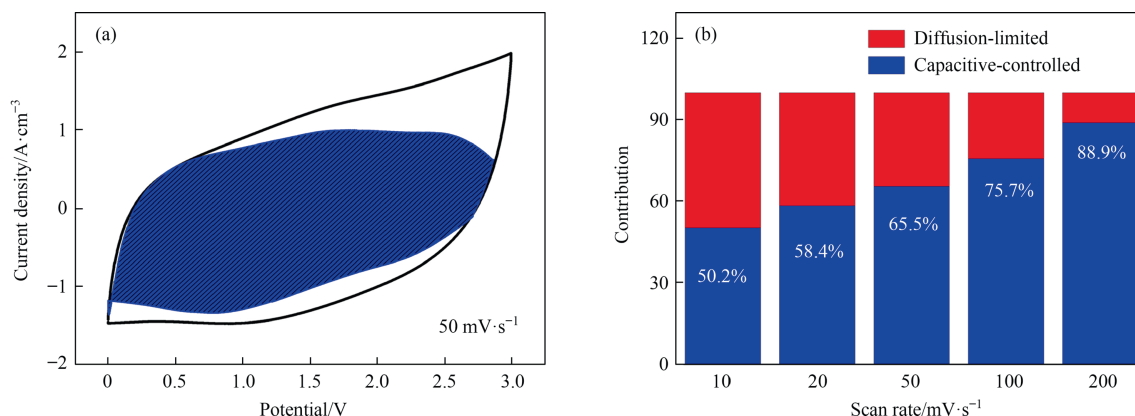


Fig. 7. (a) Voltammetric response with the shaded region showing the capacitive-controlled contribution. (b) Capacitance contribution of the wire-shaped SC at various scan rates.

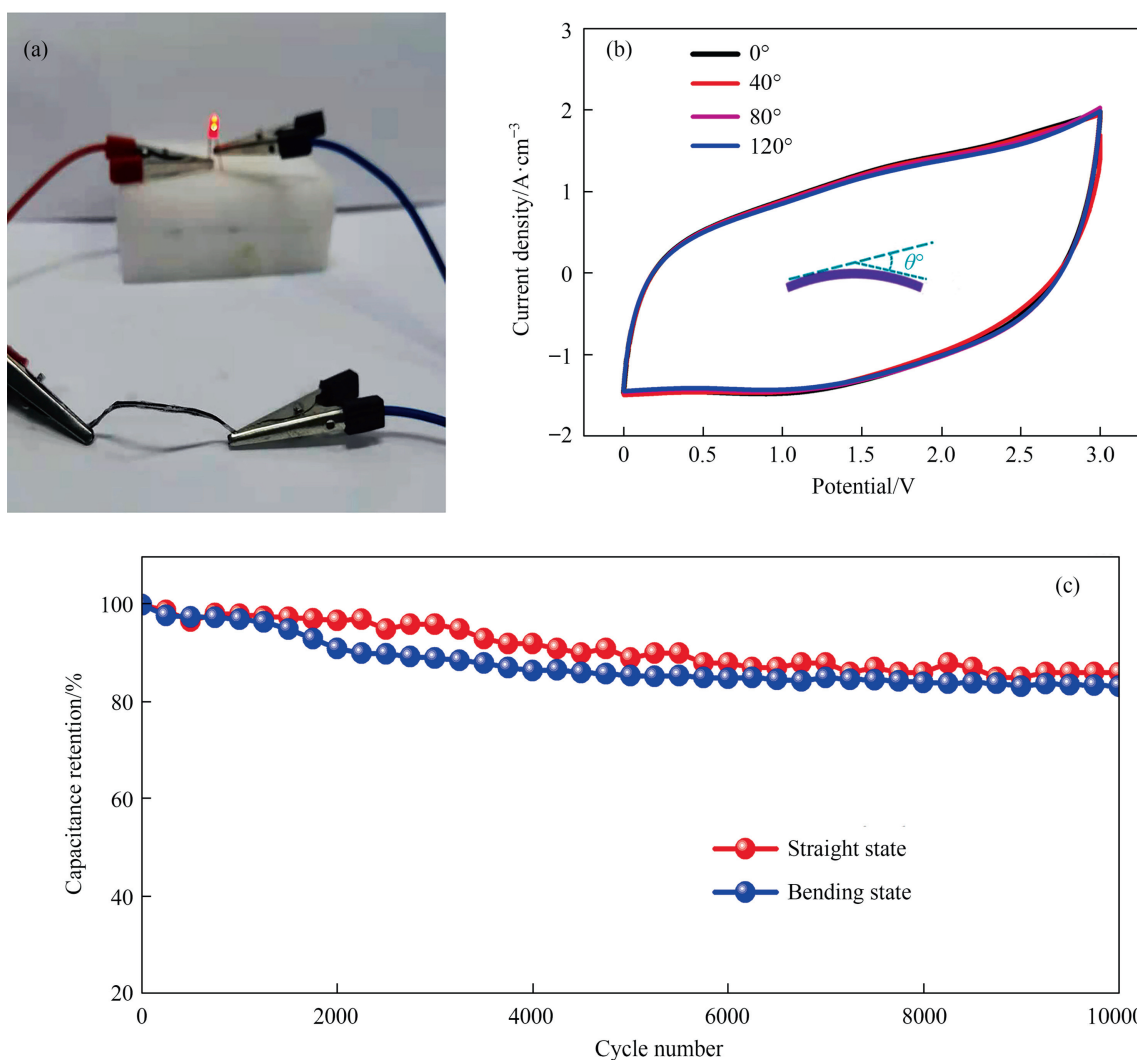


Fig. 8. (a) Digital photo showing the excellent power supply of wire-shaped SCs upon bending. (b) CV curves at 50 mV·s⁻¹ under different bending angles. (c) Long-term cycling performances of the wire-shaped SC under straight and bending states after 10,000 charging-discharging cycles.

volumetric energy density can be determined as high as 26.9 mW·h·cm⁻³, far superior to other reported wire-shaped SCs (most being <10 mW·h·cm⁻³; Table S1), even higher than dozens of commercial SCs (3.5 V/35 mF; <1 mW·h·cm⁻³), and twice as high as

4 V/500 μ A·h commercial Li-ion thin-film batteries ($\sim$ 9 mW·h·cm⁻³) [22]. Simultaneously, the maximum volumetric power density of the wire-shaped SC can reach up to 4900 mW·cm⁻³, which is equivalent to that of commercial SCs [21].

Furthermore, there is a small semicircle and an almost vertical line in the low-frequency region in the EIS plot (Fig. 6(f)), which indicates that the assembled device possesses favorable ionic diffusion and charge transport. This is mainly attributing to the high electrochemical kinetics of the FODs@GF and NCPs@GF linear electrodes in IL electrolyte. Profiting from the soft and supple structure of the device, the wire-shaped SC can be readily woven into cloth and can successfully drive electronic products (inset in Fig. 6(f)), indicating the remarkable power supply capability of the wire-shaped SC as a wearable energy storage device.

In order to estimate the charge storage process of the assembled wire-shaped SC, the diffusion-limited and capacitive-controlled processes in the total capacitance contribution were conducted in detail (Fig. 7(a) and (b)). The capacitive-controlled process can be quantitatively differentiated according to the classical Eqs. (1) and (2).

$$i = k_1 v + k_2 v^{1/2} \quad (1)$$

$$i/v^{1/2} = k_1 v^{1/2} + k_2 \quad (2)$$

By calculation, the capacitive contribution to the total current increased from 50.2% at $10 \text{ mV} \cdot \text{s}^{-1}$ to 88.8% at $200 \text{ mV} \cdot \text{s}^{-1}$, suggesting that the diffusion-limited process decreases at higher scan rates in the energy storage process of the assembled wire-shaped SC. As the scan rates exceed over $50 \text{ mV} \cdot \text{s}^{-1}$, the corresponding response comprises the surface capacitive effects rather than being diffusion-limited process, which is beneficial for achieving high power density at high current densities, confirming the superior energy-storage ability of the fabricated wire-shaped SC.

To further investigate the mechanical strength and electrochemical reliability of the wire-shaped SC, the assembled device was subsequently subjected to electrochemical behaviors under bending measurements. During static and dynamic bending, a light-emitting-diode indicator powered by the fabricated wire-shaped SC continues to emit light (Fig. 8(a) and Supplementary Movie). As displayed in Fig. 8(b), the CV curves under different bending angles (*i.e.* 0° , 40° , 80° , and 120°) exhibits similar capacitive-storage behavior to that of the straight state, which indicates that wire-shaped SC exhibits high electrochemical reliability and all-round flexibility. Furthermore, cycling performances of the wire-shaped SC under straight and bending states were also measured (Fig. 8(c)), wherein the long-term durability both exhibit high retention of about 83.7% and 80.2%, respectively. Fig. S6 shows the EIS plots of the wire-shaped SC before and after cycles, wherein the point where the high frequency region intersects the real axis generally represents the equivalent series resistance (R_s), while the diameter of the semicircle is associated with the charge transfer resistance (R_{ct}). During the charging and discharging processes, operation at high voltage approaching the upper limit voltage of the ionogel electrolyte could produce some Joule heat along with the increase in viscosity, thereby affecting the electrochemical kinetics of the wire-shaped SC. As a result, the EIS plot of the wire-shaped SC exhibits relatively higher values of R_s and R_{ct} after cycles. In this case, some capacitance would be degraded upon repeated charging-discharging processes. More information about the structure and morphology of the FODs@GF and NCPs@GF linear electrodes after 10,000 cycles are provided in Fig. S7. Therefore, the fabricated wire-shaped SC has great potential to meet the diverse needs of highly efficient energy storage in portable/wearable electronic applications.

4. Conclusions

In summary, two novel types of flexible graphene hybrid fibers, FODs@GF and NCPs@GF, have been successfully proposed via a

facile chemical reduction-induced fabrication. The synergy of the electroactive units (FODs and NCPs) and the conductive graphene nanosheets endows the FODs@GF and NCPs@GF as linear electrodes with large volumetric specific capacitance, excellent rate capability, and favorable electrochemical kinetics in IL electrolyte. For real-life applications, a high-performance wire-shaped SC using ionogel electrolyte has been assembled, for which the FODs@GF and NCPs@GF act as the negative and positive linear electrodes, respectively. The flexible and weavable wire-shaped SC delivers an ultrahigh volumetric energy density of $26.9 \text{ mW} \cdot \text{h} \cdot \text{cm}^{-3}$ and volumetric power density of $4900 \text{ mW} \cdot \text{cm}^{-3}$, and superior long-term durability over repeated 10,000 cycles in various deformation states. Considering the facile preparation technology and outstanding performance of these graphene hybrid fibers, this work provides new insight into fabricating advanced fiber electrode material for wire-shaped energy storage devices for use in portable and wearable electronics.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary Material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cjche.2021.05.045>.

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