Temperature-resistant and flexible supercapacitors based on 10-inch wafer-scale nanocarbon films

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ABSTRACT Most of the supercapacitors reported in literatures showed little or no flexibility in the working temperature around 150°C. However, the supercapacitors are generally exposed under complex system or extreme temperature, such as electric vehicles and extremely cold area. Herein, we successfully fabricated a large-scale robust nanocarbon hybrid film consisting of reduced graphene oxide (rGO), carbon nanotubes (CNTs) and MnO_x nano-flowers with the size up to 550 cm². The mechanical properties of the hybrid films depend on the ratio of CNTs. The supercapacitors prepared with the hybrid films exhibit high flexibility and keep their performances in a temperature range from −20 to 200°C. In addition, the devices display remarkable electrochemical and deformation stability at extreme temperature. This strategy has a potential for the more efficient preparation of flexible electrode materials.

Keywords: temperature-resistant, 10-inch nanocarbon film, flexible supercapacitor

INTRODUCTION

Flexible energy storage devices, such as flexible supercapacitors, play a vital role in the main electronic component due to their high-power supply capacities. Efforts have been made to improve the integrative properties for wearable devices [1–3]. Temperature-resistant property is particularly important because it deeply affects the reliability, flexibility, and electrochemical property of the supercapacitor. Most of the supercapacitors reported in literatures show little or no flexibility in the work temperature around 150°C [4,5]. Therefore, the temperature-resistant properties and

flexibility of the electrode of a supercapacitor are critical to its application in wearable devices.

Graphene has been extensively used in energy storage devices due to its unique structure and properties [6]. In particular, with its two-dimensional structure and good electrical properties, it provides adaptable alternatives to flexible devices [7]. Chemical vapor deposition graphene (CVD-G) and reduced graphene oxide (rGO) are the most well-studied electrode materials [8,9]. The CVD-G film is a suitable transparent electrode material. Considerable efforts have been made to gain the CVD-G films with the size from several square centimeters to wafer scale [10–12]. However, the active surface of CVD-G films is too low for energy storage. For example, the interfacial capacitance of the double layer at CVD-G-ionic liquid interface is only ~21 μF cm^{−2} [13]. In addition, CVD-G is usually deposited on a substrate, which complicates its fabrication [14,15]. By contrast, rGO films can be prepared by simple methods, such as immersion, rod coating, self-assembly, vacuum filtration [16–19], and possess the characteristics of free-standing, high electrical conductivity, and highly active surfaces. The vacuum filtration can produce uniform and compact, yet small films due to the complex exfoliation process and limited device sizes. The diameters of rGO films are usually ~30 mm, or wafer scale (Table S1) [20–22].

According to Shi's results [23], carbon nanotubes (CNTs) can be used to reinforce the mechanic property of rGO films. We previously reported a free-standing hybrid membrane of rGO and single-wall CNTs (rGO/CNTs) [24,25]. However, the method shows low film-forming efficiencies (1.5 inches in diameter). The specific

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capacity of supercapacitors was low and the effect of CNTs was vague. In the present work, the hybrid films could be 10 inches in size and applied as electrode materials of the flexible supercapacitor with good temperature-resistance (−20 to 200°C).

EXPERIMENTAL SECTION

Preparation of rGO/CNT/MnO_x hybrid film

The rGO/CNT hybrid films were prepared using a specially designed vacuum filtration equipment as shown in Fig. S1a. Firstly, 100 mL 2 mg mL^{−1} GO aqueous suspension was pre-reduced by 200 μL hydrazine under vigorous stirring at 90°C for 45 min. Then, 40 μL 10 wt% F127 solution and 28 mL HCl were added to the suspension. After that, 1 mg mL^{−1} CNTs aqueous solution (the ratio of rGO/CNT is adjustable) was added and stirred for 2 h. Then, the 10-inch wafer-scale hybrid film, consisting of GO, CNTs and F127, was gotten after vacuum filtration process. After annealing in a furnace at 400°C for 1 h and 900°C for 1 h, GO was reduced to rGO, and F127 was removed and rGO/CNTs nanocarbon film was obtained. MnO_x nanosheets were then electrodeposited on the rGO/CNTs hybrid film by a constant voltage method (1.5 V), where the rGO/CNTs hybrid film acted as the working electrode, an Ag/AgCl electrode was used as the reference electrode, a Pt wire was used as the counter electrode, and MnSO₄ (0.01 mol L^{−1}) was used as the electrolyte.

Preparation of [EMIM][TFSI]-containing gel electrolyte

2-Propen-1-aminium, *N,N*-dimethyl-*N*-propenyl-, chloride homopolymer (PDDA⁺Cl[−]) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) were purchased from Monils Chem. Eng. Sci. & Tech. (Shanghai) Co. Ltd. The replacement reaction happened when mixing the aqueous solution of the above two reagents. Through vacuum filtration, centrifugation and oven dry, white power was obtained. A mixture of white power and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][TFSI]) was dissolved in acetone. The solution was poured into a mold, and then the [EMIM][TFSI]-containing gel electrolyte was gotten after acetone volatilized.

Fabrication of the supercapacitor

The sandwich-structured supercapacitor consisting of two rGO/CNT/MnO_x hybrid films as electrodes and [EMIM][TFSI]-containing gel electrolyte was encapsulated with poly(dimethylsiloxane).

Characterizations

Scanning electron microscopy (SEM, LEO 1530, 5 kV) was used for morphology imaging; thermal gravimetric analysis (TGA, TA Instruments TGA 2050) for thermal stability analysis; X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi) and X-ray diffraction (XRD, Rigaku D/mass-RB) for structural and component analyses; universal testing systems (Instron 5843) for measuring the breaking strength; electrochemical test (CHI660) for the determination of electrochemical properties.

RESULTS AND DISCUSSION

The rGO/CNT hybrid films have the diameter of over 10 inches and surface area of 550 cm², seven times and fifty times greater than those of traditional films respectively (Fig. 1a). These large-scale films were free-standing and could be folded and refolded into various shapes repeatedly. The robustness of rGO/CNT hybrid films increases with the addition of CNTs, as shown in Fig. 1b. The tensile strain-stress curves were investigated under a quasi-static loading condition at the loading rate of 0.003 mm s^{−1}. All curves are divided into three stages: elastic deformation, plastic deformation, and fracture. The tensile strain-stress curves of hybrid films with different rGO/CNTs ratios are similar. At the end of elastic deformation, the crack initiates at low strength parts and propagates to the whole film with increasing load. In Fig. S1b and c, the breaking strengths of the membranes are 2, 8, 9 and 21 MPa when the rGO/CNT ratios are 1:0, 5:1, 1:5 and 0:1 respectively. According to $\sigma = E \cdot \varepsilon$ (σ is stress, E is elastic modulus, ε is strain), the elastic modulus is 152 MPa (pure rGO), 245 MPa (rGO/CNTs ratio of 5:1, 1:1, 1:5) and 290 MPa (pure CNTs), which indicates that CNTs can enhance the stiffness of hybrid films. Fig. 1c–e show that CNTs act as bridges between rGO sheets, which strengthen the hybrid membrane. Given that excess CNTs can decrease the specific surface area, the ratio of CNTs should be selectively reduced. The specific surface areas reduce from 582 to 451 m² g^{−1} with the increase of CNT content. Considering the mechanical performance and active surface, the optimal ratio of rGO/CNT is 5:1.

The pseudocapacitor electrode could combine the electrical double-layer capacitor electrode materials to enhance energy densities in favour of high electrochemical performances of supercapacitors [26–30]. Manganese oxide (MnO_x) is known as the most promising transition metal oxide material for supercapacitor electrodes due to its high specific capacitance, low cost, eco-friendliness, abundant sources and high compatibility [31–33].

Figure 1 Photographs (a), tensile strain-stress curves (b) and SEM images (c–e) of large-scale robust rGO/CNT films; SEM image (f) and high-magnification SEM image (g) of the rGO/CNT/MnO_x films.

The rGO/CNT hybrid film was then coated with MnO_x by an *in situ* electrodeposition. As shown in Fig. 1f and g, the CNTs and rGO sheets are tightly wrapped by MnO_x. The magnified image of a partial segment revealed that the MnO_x nanosheet are evenly distributed and tightly attached to the hybrid film. The phases and elemental compositions of the hybrid films were determined by XRD and XPS. The peaks for Mn 2p and Mn 1s appear at 642.2, 653.7 and 52.6 eV in the XPS spectrum of rGO/CNT/MnO_x film, which further confirms the introduction of MnO_x to the rGO/CNT film (Fig. S2a) [34]. The peaks at 531.3 and 529.8 eV in O 1s peak were attributed to the crystallization water and Mn–O [32]. The peaks at 642.2 and 653.7 eV do not match well with the binding energy of MnO, Mn₂O₃ or MnO₂, suggesting that the manganese in the hybrid film is the non-stoichiometric compound of MnO_x (Fig. S2b and c) [35–37]. As shown in Fig. S2d, the XRD patterns of rGO/CNT film and rGO/CNT/MnO_x film show that the diffraction peak of rGO/CNT is weak due to the overlapped MnO_x signal. No characteristic diffraction peak of MnO_x was observed, suggesting its amorphous feature [38].

A sandwich-structured flexible supercapacitor was

fabricated using rGO/CNT/MnO_x film as the electrodes and an [EMIM][TFSI]-containing gel as the electrolyte (Fig. 2a). The effects of MnO_x were revealed by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), electrochemical impedance spectroscopy (EIS) and cycle life curves. As shown in Fig. 2b–d, the MnO_x coating significantly increases the area of the CV curve and the discharge time of the GCD curve. The specific capacitance was increased from 30 to 60 mF cm⁻² after the electrodeposition at the current density of 0.1 mA cm⁻². These results suggest that the MnO_x coating improves the capacitance properties of the hybrid film with higher pseudocapacitance. The specific capacitance of the rGO/CNT/MnO_x hybrid film remains unchanged after 5,000 cycles, suggesting its excellent stability. Moreover, the hybrid film possesses good rate capacitance and the capacitance decreases slightly (around 37%) as the current density increases from 0.1 to 1 mA cm⁻², which reveals that the rGO/CNT acts as a connecting passage benefiting the fast electron and ion transport during the charge-discharge process.

The mass loading of MnO_x varied with the deposition time. As shown in Fig. S3, MnO_x nanosheets were

Figure 2 Schematic illustration (a) and electrochemical performance of supercapacitor based on rGO/CNT/ MnO_x films. (b) CV curves (200 mV s⁻¹), (c) GCD curves (0.1 mA cm⁻²) and (d) cycling stability and rate capacitance (inset).

continuously deposited on rGO flakes and CNT bundles, which boosted the specific capacitance. Both the area of CV curve and the discharge time of the GCD curve increased as the deposition time prolonged from 300 to 900 s. Further extending the deposition time to 1,200 s or even 1,500 s caused dramatical decrease of the films' electrochemical properties, consistent with the SEM images that the hybrid film was completely covered with MnO_x nanosheets in 1,500 s. The excess MnO_x nanosheets coating results in higher electrical resistance of the films due to the low electrical conductivity of MnO_x. On the other hand, the excess MnO_x hinders the contact of rGO/CNT films and electrolyte ions. Therefore, the optimal deposition time should be 900 s and the mass loading of MnO_x is 0.4 mg cm⁻².

Flexible supercapacitors are potential to be applied not only under ambient conditions, but also at extreme temperatures, which requires electrodes with excellent thermal stability. The thermal properties of the rGO/CNT/MnO_x hybrid films were then examined by TGA and differential thermogravimetric analysis (DTG). The rGO/CNT/MnO_x hybrid films and gel-electrolytes do not exhibit decomposition peak until 200°C (Fig. S4),

suggesting their high thermal stability. Therefore, the flexible supercapacitors prepared with rGO/CNT/MnO_x hybrid films and the gel-electrolytes were tested in two temperature-change modes: post-temperature-change test and real-time test.

For the post-temperature-change test, the supercapacitors were kept at -20 and 200°C for 10, 20 and 30 min, respectively, and then their electrochemical properties were tested. The CV curves of all supercapacitors exhibit a nearly rectangular shape at the scan rate of 20 mV s⁻¹ (Fig. 3a and b). Especially in 200°C, the area of CV curves are larger than others, because higher temperature increases the activity of ions and then increases the electrical conductivity of rGO/CNT/MnO_x. The results are in good consistence with the GCD results (Fig. S5). However, the area under the CV curves and the discharge time of GCD are alternated because temperature could slightly affect the equivalent series resistance (ESR). ESR decreased with the increase of temperature, coinciding with the EIS analysis results (Fig. S6a and b). However, the capacitive performance of the device remains in the test temperature range (Fig. S6c and d) with the frequencies up to 106 Hz and

Figure 3 Electrochemical properties of the flexible supercapacitors in two temperature-changing test modes. (a, b) Post-temperature-change test; (c, d) real-time test.

the phase angles close to -80° , similar to those of an ideal capacitor.

The real-time test was carried out in an ultra-low freezer or a heater at desired temperatures. The supercapacitors exhibit better thermal stability at 200°C than those at -20°C (Fig. 3c and d). Especially, the CV curve obtained at 200°C is similar to that obtained at room temperature (RT) with a nearly rectangular shape, while that obtained at -20°C is a bit deviated.

EIS profiles confirm the different ion transport rates within the electrodes. The EIS profiles of the supercapacitors were measured in the range from 0.01 to 106 Hz for the further investigation. The ESR room temperature at different temperatures follows the order of $-20^\circ\text{C} > \text{RT} > 200^\circ\text{C}$ (Fig. 4) due to the effects of temperature on the ion transport rate in gel-electrolyte and active electrodes. The relaxation time constant (τ_0) reflects the transition point of a supercapacitor from capacitive to resistive behavior. The maximum τ_0 at -20°C was >100 s, longer than those at 200°C (33 s) and room temperature (83 s). The short relaxation time constants indicate faster ion transport rate in the device. According to the Arrhenius law, the electrochemical

reaction and the electron transport are coupled and accelerated with the increase of temperature [25,39].

The flexibility of the prepared supercapacitor is shown in Fig. 5. Bending and curling the device did not significantly affect the CV curve, indicating its excellent flexibility and stability. In addition, the flexibility was not affected by temperature. After 200 times curls, the CV and GCD curves show no obvious deviation from the original state. Based on these results, the introduction of MnO_x enhanced the specific capacitance twice without affecting the temperature-resistant properties and flexibility of the device.

CONCLUSIONS

In summary, a 10-inch wafer-scale $\text{rGO}/\text{CNT}/\text{MnO}_x$ hybrid film was fabricated and applied as an electrode material of flexible supercapacitors. The rGO/CNT composite was integrated to provide the robustness and high conductivity of the films, and MnO_x contributed its high specific capacitance. The excellent flexibility and temperature-resistant property enabled the film applicable at wider temperatures range up to 200°C . Our work offers a complementary strategy to our previous studies

Figure 4 EIS plots (a) and the real and imaginary parts of the capacitance of flexible devices at RT, -20 and 200°C (b–d).

Figure 5 The flexibility of supercapacitors. (a) Deformation test, (b) CV curves after curling at 200°C, and (c, d) the deformation stability at 200°C.

and directs the future work towards expanding the work temperature range of flexible supercapacitors.

Received 24 December 2018; accepted 28 January 2019;
published online 27 February 2019

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Acknowledgements This work was supported by the Key Research and Development Program of Shandong Province (2017GGX20123) and the Fundamental Research Funds for the Central Universities of China (17CX02063 and 18CX02158A).

Author contributions Zang X and Hou Y designed and performed the experiments and contributed equally to this work; Wang T and Zhang R engineered the samples; Zang X wrote the paper with support from Hou Y; Zang X, Zhu H and Kang F conceived and supervised the project. All

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Supplementary information

Supporting data are available in the online version of the paper.

Conflict of interest The authors declare no conflict of interest.

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10英寸超大尺寸复合纳米薄膜用于耐温柔性超级电容器

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摘要 现有超级电容器的工作温度区间约为150°C, 但柔性较差. 在实际工作环境中, 存在一些极端的温度环境, 比如, 极寒地区. 本文制备了面积高达550 cm² (常规尺寸的29倍)的石墨烯/碳纳米管/锰氧化物复合薄膜, 并将其用于耐温柔性超级电容器. 该电极材料的性能取决于复合薄膜中石墨烯、碳纳米管和锰氧化物的比例. 此柔性超级电容器可在-20~200°C温度区间内保持良好的电化学性能和柔性, 表现出优异的稳定性. 本文为复合纳米材料薄膜的大批量制备和适用于宽温度区间的柔性超级电容器的发展奠定了基础.