Scalable synthesis of hierarchically structured carbon nanotube–graphene fibres for capacitive energy storage

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Micro-supercapacitors are promising energy storage devices that can complement or even replace batteries in miniaturized portable electronics and microelectromechanical systems. Their main limitation, however, is the low volumetric energy density when compared with batteries. Here, we describe a hierarchically structured carbon microfibre made of an interconnected network of aligned single-walled carbon nanotubes with interposed nitrogen-doped reduced graphene oxide sheets. The nanomaterials form mesoporous structures of large specific surface area (396 m² g⁻¹) and high electrical conductivity (102 S cm⁻¹). We develop a scalable method to continuously produce the fibres using a silica capillary column functioning as a hydrothermal microreactor. The resultant fibres show a specific volumetric capacity as high as 305 F cm⁻³ in sulphuric acid (measured at 73.5 mA cm⁻² in a three-electrode cell) or 300 F cm⁻³ in polyvinyl alcohol (PVA)/H₃PO₄ electrolyte (measured at 26.7 mA cm⁻² in a two-electrode cell). A full micro-supercapacitor with PVA/H₃PO₄ gel electrolyte, free from binder, current collector and separator, has a volumetric energy density of ~6.3 mWh cm⁻³ (a value comparable to that of 4 V–500 μA h thin-film lithium batteries) while maintaining a power density more than two orders of magnitude higher than that of batteries, as well as a long cycle life. To demonstrate that our fibre-based, all-solid-state micro-supercapacitors can be easily integrated into miniaturized flexible devices, we use them to power an ultraviolet photodetector and a light-emitting diode.

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T he continued miniaturization of portable electronics requires energy storage devices with large volumetric energy densities.¹–⁴ Although suffering from sluggish charge/discharge processes and limited cycle life, microbatteries currently remain the device of choice for this type of application. Micro-supercapacitors (micro-SCs)⁵,⁶ are promising alternatives as they can provide higher power densities, faster charge/discharge rates and much longer lifetimes.²,⁵ However, the key challenge for their use in practical applications is increasing their energy density to values close to and even exceeding those of microbatteries without compromising other electrochemical characteristics.¹,²,⁶ To this end, electrodes with large volumetric capacitance need to be developed. Materials with high electrical conductivity and accessible surface area can achieve high electrical double layer (EDL) capacitances, which can then be further enhanced by means of the pseudocapacitance associated with surface functional groups and/or pseudocapacitive components.⁷,⁸ Although various thin-film micro-SCs based on transition metal oxides⁹ and conducting polymers¹⁰,¹¹ have recently been fabricated using printing, lithography and laser writing,¹² these devices often suffer from short cycle lives, low stability and poor rate capability. In an alternative approach, micro-SCs based on carbon nanomaterials, including carbon onion¹³, reduced graphene oxide (rGO),¹⁴ carbide-derived carbon,¹⁵ graphene dots¹⁶ and carbon nanotube (CNT)/rGO composites¹⁷,¹⁸ have exhibited excellent rate capabilities and stability, but low volumetric energy density. Recently, fibre-shaped micro-SCs have been developed for flexible and wearable electronics¹⁹, based on carbon fibres,¹⁶,¹⁷, rGO fibres¹⁸ and even carbon-based composite fibres containing pseudo-capacitive materials.¹⁹–²² In all cases, however, it remains challenging to increase the volumetric energy density of micro-SCs without sacrificing device power density and cycle life.

A general strategy to increase volumetric energy density is to develop porous conductive electrode materials with sufficiently high packing density to maximize the utilization of the limited volume of a micro-SC. In this context, graphene sheets are widely regarded as a promising electrode material because they have ultrahigh surface area and excellent conductivity as well as high mechanical and chemical stability. Graphene can be assembled into various interesting structures, including one-dimensional fibres, two-dimensional films and three-dimensional foams, which can demonstrate high gravimetric capacitances but poor volumetric performances. A possible explanation of this behaviour lies in the strong intersheet π–π interaction, which, while increasing the packing density, does not allow high ion accessibility. To reduce stacking, graphene–CNT composites have been proposed and fabricated. In particular, two-dimensional CNT/rGO hybrid films and three-dimensional vertically aligned CNT/graphene pillars have shown significantly improved electrochemical performances. For practical applications, however, their volumetric energy densities would still need to be improved significantly.²⁶–²⁸

Here, we describe the scalable synthesis of a hierarchically structured carbon microfibre made of a single-walled carbon nanotube (SWNT)/nitrogen-doped rGO sheet interconnected network architecture that shows excellent electrical conductivity and high packing density while maintaining a large ion-accessible surface.
area. Micro-SCs fabricated with these fibres show volumetric energy densities comparable to those of thin-film lithium batteries, without compromising cyclability and rate capability.

**Synthesis of carbon hybrid microfibres**

Hydrothermal processes are widely used to synthesize materials in high-temperature aqueous solutions at high vapour pressures using pressure vessels called autoclaves. Fused silica capillary columns are generally used for chromatographic separation, which, unlike fragile glass tubes, are flexible and have good high-temperature and pressure tolerance. We employed a fused-silica capillary column as a hydrothermal microreactor for the scalable production of SWNT/rGO fibres, as shown in Fig. 1a. Nitric-acid-treated SWNTs and GO (Supplementary Fig. 1) were combined to form hybrid microfibres in the presence of ethylenediamine (EDA) as the nitrogen dopant to dope GO with concomitant reduction during the hydrothermal process. By so doing, we took advantage of the following synergistic effects. First, GO is a good surfactant with which to disperse SWNTs, while SWNTs hinder the restacking of GO, resulting in a homogeneous aqueous suspension. Second, heteroatom doping not only improves surface conductivity and wettability, but also induces pseudocapacitance in carbon nanomaterials. More importantly, EDA, with its two $-\text{NH}_2$ end groups, can act as a molecular ‘end-anchoring’ reagent to bind acid-oxidized SWNTs and GO to create the three-dimensional pillared vertically aligned SWNT/rGO architectures via self-assembling within the fibre confinement, which is oriented along the fibre length (Fig. 2g–i) by the shear force while flowing through the silica capillary column. Within the SWNT/rGO assemblies, the aligned SWNTs, which have a relatively low EDL capacitance, have excellent electrical conductivity and provide an outstanding rate capability, while the large-surface-area rGO offers a high EDL capacitance (theoretically, $550 \text{ F g}^{-1}$). These synergistic effects are responsible for the enhanced electrochemical performances observed from our hybrid fibres.

Owing to the small size and mechanical flexibility of the silica capillary columns, multiple long columns can be integrated with a valve switching system for continuous fibre production. As a proof-of-concept study, two 5-m-long capillary columns were used to produce 50-m-long fibres in 48 h, suggesting a production yield of $1 \text{ m h}^{-1}$ (Supplementary Fig. 2). The production rate was tunable by adjusting the synthesis conditions.

To identify the optimum composition of the hybrid fibres for micro-SC applications, several fibres with different SWNT/GO mass ratios of 0:1, 1:8, 1:4 and 1:1 (denoted rGO fibre, fibre-1, fibre-2 and fibre-3, respectively) were produced. The continuous fibres could not form when the mass fraction of GO was below 50 wt% (Supplementary Fig. 3). The as-synthesized wet fibres ($260–300 \mu\text{m}$ in diameter) were dried in air for 4 h, resulting in a five- to sixfold shrinkage in diameter to $40–60 \mu\text{m}$ due to the capillary force during water evaporation (Table 1).

**Structural characterization of carbon hybrid microfibres**

The as-prepared dry hybrid fibres exhibited good tensile strength (84–165 MPa, Supplementary Fig. 4), comparable to those of wet-spun rGO and SWNT fibres. They were also flexible, and could be bent into different shapes or woven into textile structures (Fig. 1d–f). The high packing density and large ion-accessible
surface area are two prerequisites for SC electrodes to achieve high volumetric performance\textsuperscript{7,8}. It was noted that both the density and surface area of our fibres increased with increasing SWNT fraction (Table 1) due to the aforementioned unique multiscale hierarchical structure, as revealed by scanning electron microscopy (SEM).

SEM images (Fig. 2a–c) show that the rGO fibre has densely stacked rGO sheets that are aligned along its main axis as a result of capillary forces during the drying process. Such dense stacking of the rGO leads to low accessible surface areas\textsuperscript{38}. In contrast, the specific surface areas of the hybrid fibres increased from 24 m\textsuperscript{2} g\textsuperscript{−1} to 396 m\textsuperscript{2} g\textsuperscript{−1} with increasing SWNT fraction from 0 to 50\% (Table 1). The hybrid fibres have an interconnected porous structure (Fig. 2d–f). The aligned SWNTs interposed between the rGO layers not only reduce the stacking of the rGO, but also provide well-developed porosity in the hybrid fibre (Fig. 2g–i). As a result, fibre-3 has a specific surface area of 396 m\textsuperscript{2} g\textsuperscript{−1}, much higher than those of carbon-based fibres reported so far, including rGO fibre (18 m\textsuperscript{2} g\textsuperscript{−1})\textsuperscript{38}, multiwalled CNT (MWCNT)-coated rGO fibre (89 m\textsuperscript{2} g\textsuperscript{−1})\textsuperscript{34}, dry-spun MWCNT fibre (100 m\textsuperscript{2} g\textsuperscript{−1})\textsuperscript{16}, carbon microfibre (3.4 m\textsuperscript{2} g\textsuperscript{−1})\textsuperscript{39}, and wet-spun SWNT fibre (160 m\textsuperscript{2} g\textsuperscript{−1})\textsuperscript{40}. The nitrogen adsorption-desorption isotherm of fibre-3 (Supplementary Fig. 5a) has a hysteresis loop, suggesting its mesoporous structure. The pore size distribution obtained from the Barrett–Joyner–Halenda method\textsuperscript{41} ranges from \( \approx 1.5 \) to 18 nm with a peak at \( \approx 5 \) nm (Supplementary Fig. 5b). Such a mesoporous structure is beneficial in providing a large accessible surface for fast ion transport. Therefore, it is the three-dimensional pillared vertically aligned SWNT/rGO assemblies confined within a one-dimensional fibre-like architecture that makes our fibres have both the high packing density and large ion-accessible surface area that are attractive for high-volumetric-performance SCs. For the hybrid fibres with a high SWNT fraction, SWNT alignment could be further enhanced by the inter-tube hydrogen-bonding interaction between the hydroxyl groups along the sidewalls of acid-treated SWNTs\textsuperscript{42}. When noticed that when the fraction of SWNTs is low, a SWNT network could still form, albeit with a poor alignment along the fibre axis direction (Supplementary Fig. 6).

The fibres are susceptible to nitrogen doping during hydrothermal synthesis in the presence of EDA (Table 1), as confirmed by energy-dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy, electron energy loss spectroscopy and Fourier-transform infrared spectroscopy (Supplementary Figs. 7–11). It was found that EDA reacted with both the GO and acid-treated SWNTs via...
amide–bond linkage\textsuperscript{39,43}. Nitrogen was doped into the rGO framework as pyridinic and pyrrolic N (Supplementary Fig. 8e) during the hydrothermal process\textsuperscript{29}, but nitrogen doping to the acid-treated SWNTs was negligible (Supplementary Fig. 10), most probably because of the relatively low density of the surface carboxylic groups on the SWNTs. SWNT incorporation, coupled with nitrogen doping of rGO, significantly improved the electrical conductivity of the hybrid fibres (Supplementary Fig. 12). Hence, fibre-3 has a conductivity of 102 S cm\textsuperscript{-1}, which is about eight times higher than that of the rGO fibre (12 S cm\textsuperscript{-1}) and much better than those of previously reported rGO\textsuperscript{44} and CNT fibres\textsuperscript{45,46}. Furthermore, our hybrid fibres showed negligible change in electrical conductivity over 1,000 bending cycles (Supplementary Fig. 12d), demonstrating their excellent structural stability.

**Electrochemical characterization of fibre electrodes**

We firstly tested the electrochemical performance of the as-synthesized fibres in a three-electrode cell in H\textsubscript{2}SO\textsubscript{4}. Their cyclic voltammetry (CV) curves at scan rates in the range 2–200 mV s\textsuperscript{-1} and galvanostatic discharge curves at various current densities are shown in Fig. 3a and Supplementary Figs 13 and 14. The CV curves show reversible cathodic and anodic peaks at 0.3–0.5 V versus Ag/AgCl (Fig. 3a), indicating the presence of pseudocapacitance. The redox peaks disappear in neutral electrolyte (1 M LiClO\textsubscript{4}) (Fig. 3c, Supplementary Fig. 15), suggesting that the pseudocapacitance was induced by oxygen-containing functional groups and/or nitrogen heteroatoms\textsuperscript{46}. The enhanced capacitive performance induced by nitrogen doping was further confirmed by comparative CV curves of the fibres with and without nitrogen doping (Supplementary Fig. 16). The specific volumetric capacitance (C\textsubscript{sp}) of the fibres was calculated using their galvanostatic discharge curves (Fig. 3b). It was found that fibre-3 has the highest specific volumetric capacitance of \(\sim 305 \text{ F cm}^{-3}\) at \(\sim 73.5 \text{ mA cm}^{-2}\) in 1 M H\textsubscript{2}SO\textsubscript{4} in the three-electrode cell (or \(\sim 300 \text{ F cm}^{-3}\) at \(\sim 26.7 \text{ mA cm}^{-2}\) in polyvinyl alcohol (PVA)/H\textsubscript{2}PO\textsubscript{4} electrolyte in a two-electrode cell, see below). To our knowledge, this is one of the highest values of specific volumetric capacitance among all reported porous carbon materials (Supplementary Table 1).

The observed large volumetric capacitances of the hybrid fibres can be attributed to the synergistic effect associated with their multi-scale hierarchical structures, in which rGO provides a large surface area for ion adsorption while the highly conductive aligned SWNT network reduces the rGO interlayer resistance and contact resistance with external circuits. Electrochemical impedance spectroscopic measurements show that the hybrid microfibres have much smaller equivalent series resistances than the rGO fibre (from the X-intercept of the Nyquist plot, Fig. 3d), and a nearly vertical line at the end of the semicircular region seen for fibre-3 (Fig. 3d). SWNT incorporation can reduce the stacking of the rGO to provide a large surface area with well-defined mesoporosity for efficient electrolyte penetration and ion adsorption, while increasing the bulk density of fibre-3 to \(\sim 0.6 \text{ g cm}^{-3}\), which is twice that of common graphene materials (\(\sim 0.3 \text{ g cm}^{-3}\), 60–100 F cm\textsuperscript{-3}\)\textsuperscript{17}. It was estimated that \(\sim 40\%\) of the total capacitance of fibre-3 arises from the pseudocapacitance (Supplementary Fig. 17). The presence of oxygen-containing functional groups and nitrogen heteroatoms in the hybrid fibres increases their surface wettability (small contact angle of 53°, Supplementary Fig. 18), which enhances polar interactions with the electrolyte solution\textsuperscript{13}. This is not inconsistent with the smaller volumetric capacitance determined in the neutral electrolyte (Supplementary Fig. 15), in which the surface functional groups are not sufficiently polarized.
Testing of all-solid-state micro-SCs

We used fibre-3 (with the best capacitive performance measured in the three-electrode cell) as both active materials and current collectors to construct flexible micro-SCs (Fig. 4a). Typically, two parallel fibre-3 electrodes were mounted onto a flexible polyester (PET) substrate using PVA–H3PO4 electrolyte without binder, current collector, separator or any packaging material (see Supplementary Fig. 19 for a detailed description). The total volume of each micro-SC, including two fibres and the surrounding solid electrolytes, was estimated to be $\sim 7.5 \times 10^{-2} \text{cm}^3$. The CV curves of the micro-SC at various scanning rates (5–100 mV s$^{-1}$) have an almost rectangular shape within 0–1 V (Supplementary Fig. 20). Its galvanostatic charge/discharge curves (Fig. 4b) have a triangular shape with a coulombic efficiency of $\sim 98\%$, indicating excellent reversibility and good charge propagation between the two fibre electrodes. Figure 4c illustrates that the volumetric capacitance of the micro-SC ($C_{\text{el},V}$, normalized to the whole device volume) is $\sim 45.0 \text{ mF cm}^{-3}$ at $\sim 26.7 \text{ mA cm}^{-2}$ and $\sim 25.1 \text{ F cm}^{-3}$ at $\sim 800 \text{ mA cm}^{-2}$, corresponding to area capacitances ($C_{\text{el},A}$) of $\sim 116.3 \text{ mF cm}^{-2}$ and $\sim 64.6 \text{ mF cm}^{-2}$, respectively, outperforming all previously reported carbon-based micro-SCs with capacitances in the range of 1–18 F cm$^{-3}$ or 0.5–86 mF cm$^{-2}$ (Supplementary Tables 2 and 3). The specific volumetric capacitance of a single-fibre electrode ($C_{\text{el}}$) in a two-electrode cell was calculated using galvanostatic discharge curves to be $\sim 300 \text{ F cm}^{-3}$ at $\sim 26.7 \text{ mA cm}^{-2}$ (Supplementary Table 2). Figure 4d shows that the micro-SC retains 93% of its initial capacitance after 10,000 charge/discharge cycles, demonstrating its impressive performance stability with a long cycle life, as is the case for other nitrogen-doped graphene materials $^{48}$. The volumetric power/energy density of the whole SC is a more meaningful parameter for evaluating the energy storage performance of the microdevice than the gravimetric power/energy density based on active electrode materials $^{8}$. The Ragone plots in Fig. 4e compare the volumetric performance of our micro-SCs to those of commercially available energy-storage devices. Our micro-SC has a volumetric energy density ($E_{\text{cell},V}$, normalized to the whole device volume) of $\sim 6.3 \text{ Wh cm}^{-3}$, which is about ten times higher than the energy densities of commercially available supercapacitors ($2.75 \text{ V/44 mF}$ and $5.5 \text{ V/100 mF}$, $\sim 1 \text{ mWh cm}^{-3}$) $^{3,6}$ and even comparable to the $4 \text{ V/500 mAh}$ thin-film lithium battery (0.3–10 mWh cm$^{-3}$) $^{3}$. This energy density value is also higher than that of recently reported thin-film supercapacitors based on different two-dimensional materials, including laser-scribed graphene ($\sim 1.36 \text{ mWh cm}^{-3}$ in ionic liquid) $^{6}$ and transition-metal carbides and carbonitrides ($\text{Ti}_2\text{C}_2$ MXenes, $\sim 1 \text{ mWh cm}^{-3}$ in K$_2\text{SO}_4$) $^{47}$, and comparable to that of macroscale SCs based on graphene-derived three-dimensional porous carbon $^{89}$. The maximum volumetric power density ($P_{\text{el},V}$) for our micro-SCs is 1.085 mW cm$^{-3}$, comparable to the commercially available supercapacitors and more than two orders of magnitude higher than that of lithium thin-film batteries $^{6}$. To our knowledge, the volumetric energy density in this work is the highest value among all carbon-based solid-state micro-SCs reported to date (Supplementary Tables 2 and 3).

The micro-SC was further subjected to mechanical bending tests. It shows negligible capacitance change ($<0.05\%$) on bending to 90° (Supplementary Fig. 21). Furthermore, it retains more than 97% of its initial capacitance after bending 1,000 times at 90° (Fig. 4f), demonstrating the high flexibility and electrochemical stability desirable for flexible electronics.

Use of multiple micro-SCs to power nanosystems

To meet specific energy and power needs for practical applications, three micro-SCs were assembled in series (Fig. 5a,b) and in parallel (Fig. 5c,d). Compared with a single micro-SC with an operating voltage of 1.0 V, the three micro-SCs connected in series...
exhibited a 3 V charge/discharge voltage window (Supplementary Fig. 22) with similar discharge time (Fig. 5b). The output current of the parallel micro-SC assembly increased by a factor of three and its discharge time is three times that of a single micro-SC when operated at the same current density (Fig. 5d, Supplementary Fig. 23). Moreover, multiple micro-SCs were assembled in parallel by incorporating a different number of fibres (up to 40 fibres) (Fig. 5e,f). The overall capacitance of the assembled micro-SCs increased linearly with the number of fibres, showing good scalability.

To further demonstrate the potential applications of the fibre-based micro-SCs as efficient energy storage components for electronic and optoelectronic devices, we constructed a self-powered nanosystem, in which three fully charged micro-SCs were assembled in series to power an ultraviolet photodetector based on TiO$_2$ nanorod arrays grown on a fluorine-doped tin oxide (FTO) glass substrate$^{50}$ without any external bias voltage (Fig. 5g). Using the integrated micro-SCs as the external power source, the photodetector has a steady response to ultraviolet light irradiation ($\lambda = 254$ nm), as shown in Fig. 5h. Fully charged integrated micro-SCs with a 3 V charge/discharge voltage window were used as the power source for this photodetector.
multiple micro-SCs can also be used to power a light-emitting diode, as shown in Supplementary Fig. 24.

Conclusions

Using a silica capillary column as a linear hydrothermal microreactor, we have developed a scalable method to continuously produce carbon microfibres with hierarchical structures comprising nitrogen-doped rGO and acid-oxidized SWNTs. Directed assembly of these two carbon components within the microfibre confinement in the presence of ethylenediamine led to the formation of three-dimensional pillarated assemblies along the fibre length. The resultant hybrid fibre exhibits high packing density and large ion-accessible surface areas, as is desirable for high-volumetric-performance micro-SCs. Our fibre has a conductivity of 102 S cm\(^{-1}\) and a specific surface area of 396 m\(^2\) g\(^{-1}\). We have shown that the capacitor electrodes fabricated from these fibres have a specific volumetric capacity of 305 F cm\(^{-3}\) in H\(_2\)SO\(_4\) (at 73.5 mA cm\(^{-3}\), in a three-electrode cell) and 300 F cm\(^{-3}\) in PVA/H\(_2\)PO\(_4\) (at 26.7 mA cm\(^{-3}\), in a two-electrode cell). An all-solid-state micro-SC made from two such parallel fibre electrodes on a flexible polymer substrate, using PVA/H\(_2\)PO\(_4\) as the gelled electrolyte, without binder, current collector, separator or any other packaging material, exhibited a long cycle life (93% device capacitance retention over 10,000 cycles) and an ultrahigh volumetric energy density of \(\sim 6.3 \text{ mWh cm}^{-3}\), about tenfold higher than those of state-of-the-art commercial supercapacitors and even comparable to the 4 V/500 \(\mu\)Ah thin-film lithium battery. The micro-SC delivers a maximum power density of up to 1,085 mW cm\(^{-3}\), a value comparable to that of typical commercially available supercapacitors and more than two orders higher than the power density of lithium thin-film batteries. Our micro-SCs can be integrated either in series or in parallel to meet the energy and power needs in various potential applications, including portable flexible optoelectronics, multifunctional textiles, sensors and energy devices, as exemplified in this study by powering a TiO\(_2\)-based ultraviolet photodetector and a light-emitting diode. Our device could bridge the energy density gap between microbatteries and micro-SCs for multifunctional textiles, sensors and energy devices, as exemplified in this study by powering a TiO\(_2\)-based ultraviolet photodetector and a light-emitting diode. Our device could bridge the energy density gap between microbatteries and micro-SCs for multifunctional textiles, sensors and energy devices.

Fabrication and characterization of all-solid-state micro-SCs. The polymeric gel electrolyte (PVA/H\(_2\)PO\(_4\)) was prepared according to a previously reported method\(^\text{29}\) (Supplementary Methods 2). Two dry fibres with the same length and from the same synthesis batch were immersed in the PVA/H\(_2\)PO\(_4\) electrolyte solution for 5 min. Thereafter, the electrolyte wetted fibres were placed on a PET film, in parallel, and their position was adjusted under an optical microscope (HI-Scope Advanced KH-3000, X700). Finally, the assembled device was dried under ambient conditions until the PVA/H\(_2\)PO\(_4\) gel solidified. The performance of the assembled micro-SCs was evaluated by CV and galvanostatic charge/discharge in a two-electrode configuration using the potentiostat (CHI 660D). Two commercial capacitors were also tested, including a supercapacitor (NEC Tokin, 5.5 V 0.1 F) and an aluminium electrolytic capacitor (Mouser Electronics, 75-TE1066-E3, 3 V, 300 \(\mu\)F). The capacitance of the supercapacitors \((C_{\text{SC}})\) in a two-electrode cell was calculated from their galvanostatic charge/discharge curves at different current densities using

\[
C_{\text{SC}} = i/(dV/dt)
\]

where \(i\) is the discharging current and \(dV/dt\) is the slope of the discharge curve. Alternatively, \(C_{\text{SC}}\) can also be calculated from CV curves using

\[
C_{\text{SC}} = Q/2V = \int_{V_{\text{cell}}}^{V_{\text{cell}}} \frac{i}{V} \, dV
\]

where \(Q\) is the total voltammetric charge obtained by integrating the positive and negative sweeps \((i(V)\) is the current\) in a CV curve, \(V\) is the scan rate, and \(V(V_{\text{cell}},-V_{\text{cell}})\) represents the scanned potential window of 0.9 V used in the three-electrode cell in this study.

Methods

Synthesis of carbon hybrid fibres. GO was prepared from natural graphite flakes by a modified Hummers’ method, as previously described\(^\text{31}\). SWNTs (Carbon Solution, AP-SWNT, with diameters around 1.4 nm) were oxidized by nitric acid reflux for 4 h. The homogenous acid-oxidized SWNT/GO aqueous dispersions at different SWNT/GO mass ratios of 1:1.4 and 1:1.1 were prepared by adding a predetermined amount of functionalized SWNTs into 5 ml GO aqueous solution (8 mg ml\(^{-1}\)) followed by the addition of 5 \(\mu\)l EDA. The dispersion was injected into a flexible fused-silica capillary column (0.5 mm inner diameter; Biotac, BT-G-530600) by a peristaltic pump (Shimadzu, LC-20AT). The capillary column was placed in a furnace with one end connected to the peristaltic pump and a nitrogen cylinder through a three-way valve, and the other end terminated by a one-way valve. Because of their flexibility and thermal stability, a long column (up to metres) can be easily packed into a small furnace. The capillary column served as a hydrothermal reactor, and was heated at 220 °C for 6 h with both valves closed. After cooling to room temperature, the resultant wet fibre was washed out by nitrogen flow into a water reservoir. Thereafter, the wet fibre was dried in air for 4 h.

Electrochemical characterization of individual fibres. A three-electrode cell, consisting of an Ag/AgCl (3 M KCl) electrode as the reference electrode, a platinum wire as the counter electrode and a single fibre as the working electrode in 1 M H\(_2\)SO\(_4\) or LiClO\(_4\) electrolyte, was used for capacitance measurements by a potentiostat (CHI 660D). The specific volumetric capacitance \(C_v\) of the fibres in a three-electrode cell was calculated according to

\[
C_v = C_{\text{electrode}}/V_{\text{fibre}}
\]

where \(C_{\text{electrode}}\) is the measured capacitance in the three-electrode configuration and \(V_{\text{fibre}}\) is the volume of the fibre used as the working electrode. The fibre is considered to be a cylinder to calculate its volume. \(C_{\text{electrode}}\) was calculated from the galvanostatic discharge curves, using the equation

\[
C_{\text{electrode}} = i/(dV/dt)
\]

where \(i\) is the discharging current, and \(dV/dt\) is the slope of the discharge curve. Alternatively, \(C_{\text{electrode}}\) was also calculated using the voltammetric charge integrated from CV curves according to the formula

\[
C_{\text{electrode}} = \frac{Q}{2V} = \frac{1}{2V} \int_{V_{\text{cell}}}^{V_{\text{cell}}} \frac{i}{V} \, dV
\]

References


CORRIGENDUM

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