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Energy materials

Hierarchical core–shell Co_3O_4/graphene hybrid fibers: potential electrodes for supercapacitors

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ABSTRACT

Toward the fast development of portable devices, the lightweight, flexible, and even wearable energy storage devices are very required. One effective device is the graphene-based fiber supercapacitors. Here we present the core–shell Co_3O_4/graphene hybrid fibers by hydrothermal method for the first time, where Co_3O_4 directly grows on the surface of graphene forming excellent hierarchical nanostructures. The combination of the Co_3O_4 shell and graphene core evidently improves the capacitive behaviors of the hybrid fibers. The Co_3O_4/graphene hybrid fibers are lightweight, flexible, and wearable, showing ultrahigh electrochemical performances such as large specific capacitance of 236.8 F g^{-1} (196.3 mF cm^{-2}) at current density of 0.2 A g^{-1}, outstanding rate capability, and excellent cycling stability (72.7% retention after 10000 cycles). The high electrochemical performances reveal the great potential of core–shell Co_3O_4/graphene hybrid fibers as electrodes in the energy storage system.

Introduction

As the portable devices become an important trend, the requirement of flexible energy storage devices is very necessary [1]. In order to realize large-scale integration, the energy storage devices such as supercapacitors should be lightweight, small-sized, and flexible as much as possible [2–5]. However, the supercapacitors based on conventional materials and structures are heavy and hard, which are not suitable for large-scale integration of portable electronic devices [6, 7]. Recently, much efforts have been made to explore lightweight and flexible supercapacitors with the planar [8, 9] and fiber-shaped structures [2, 3]. They maintain good electrochemical performances, even after high mechanical bending and twisting. Compared with the planar ones, the fiber-shaped supercapacitors have advantages in flexibility, easiness to be woven into textiles, and thus are promising for wearable electronic devices.

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In the last decade, various fibers based on carbon materials have been investigated for flexible supercapacitors [10–16]. In recent years, the emphasis has been placed on the improvement of both energy and power densities of devices [15, 17]. As compared to carbon and carbon nanotube fibers, the graphene fibers exhibit relatively high electrochemical behaviors due to the high specific surface area and electric conductivity of graphene. Meanwhile, it is convenient to produce graphene fibers by such methods as wet-spinning through injecting graphene oxide (GO) dispersion into a coagulation bath and then reducing [18–20]. Hence, the graphene-based fibers will certainly be very promising in wearable electrochemical devices.

For practical applications of supercapacitors, an effective strategy is to combine carbon materials with transition metal oxides [21–24], which may possess both high conductivity and capacitance and so have high power and energy densities. Among transition metal oxides hotly studied, cobalt oxide (Co_3O_4) has attracted considerable attention due to its rather high capacitance for pseudocapacitor electrodes [11, 25, 26]. Recently, the enhanced electrochemical performances of graphene fiber-based electrodes have been demonstrated by decorating the graphene with transition metal oxides such as MnO_2 [27–29]. In theory, the decoration of Co_3O_4 on graphene fibers is expected to have much high electrochemical behaviors. However, few reports on this issue have appeared so far.

In this work, we provide a simple hydrothermal process to grow Co_3O_4 nanostructures directly on the surface of graphene fibers, forming a hierarchical core–shell structure of Co_3O_4/graphene hybrid fibers. Quite different from the core–shell hybrid fibers previously reported [27–29], the Co_3O_4 shell is not simply coated on the graphene core forming a flat layer without any nanotopography; in contrary, the Co_3O_4 directly grows from the surface of reduced graphene oxide (RGO) fibers, having excellent double nanostructures of nanosheets and nanowires, which can provide much large surface area of active materials. The Co_3O_4/graphene hybrid fibers exhibit a high specific capacitance of 236.8 F g^{-1} (196.3 mF cm^{-2}, 165.7 F cm^{-3}) at the current density of 0.2 A g^{-1}, good rate capability, and long cycle stability (72.7% retention after 10000 cycles). The present studies reveal that the hierarchical core–shell Co_3O_4/graphene hybrid fibers are very potential as high-performance electrodes for supercapacitors (e.g., coiled yarn supercapacitors).

Experimental

The GO fibers were prepared by using a wet-spinning method. The GO aqueous dispersion was first concentrated by centrifugation at 15000 rpm for 1 h and then under ultrasonication treatment for 30 min, so the GO spinning dope (10 mg mL^{-1}) was obtained. The GO spinning dope (2 mL) was injected into a coagulation bath (5 wt% $CaCl_2$/ethanol solution) with an injection speed of 200 μL min^{-1}. The obtained fibers were washed three times with ethanol and deionized water, respectively. The GO fibers were collected onto the graphite roller and then dried at 60 °C for 12 h. The GO fibers were first treated by HI at 100 °C for 8 h, and subsequently they were annealed at 1000 °C for 4 h in the H_2/Ar (1:4 of volume ratio) atmosphere. Finally, the RGO fibers were obtained after being naturally cooled to room temperature. After weighing, the linear density of the RGO fibers could be calculated as 11.23 μg cm^{-1}.

The 0.997 g of $Co(CH_3COO)_2$, 0.168 g of NH_4F, and 1.201 g $CO(NH_2)_2$ were dissolved in 40 mL of deionized water. The solution was stirred for 2 h at room temperature. The RGO fibers were suspended in a 50-mL Teflon-lined autoclave. Then, the solution was transferred to the autoclave. The hydrothermal treatment was carried out at 120 °C for 5 h. The samples were washed in ethanol and deionized water. They were annealed at 300 °C to obtain the core–shell structure Co_3O_4/graphene hybrid fibers. After weighing, the linear density of the hybrid fibers could be calculated as 18.19 μg cm^{-1}. Per centimeter of the RGO fibers had been loaded 6.96 μg of Co_3O_4. In the Co_3O_4/graphene hybrid fibers, the mass ratio of the Co_3O_4 and the RGO fiber is about 5:8.

The structures of Co_3O_4/graphene hybrid fibers were investigated by a HITACHI S4800 scanning electron microscope (SEM). The compositions of hybrid fibers were measured by X-ray energy-disperse spectra (EDS) in an Oxford Instruments EDS System and X-ray photoelectron spectroscopy (XPS) spectra with a Thermo ESCALAB-250 spectrometer using an Al Kα radiation (E = 1486.6 eV). The Raman spectra were recorded on a LabRAM HR Evolution spectroscopy with argon-ion laser (514.5 nm).

The electrochemical performances were measured at room temperature on the CHI760E electrochemical workstation, including cyclic voltammetry (CV), galvanostatic charge–discharge (GCD), and electrochemical impedance spectroscopy (EIS). The aqueous electrolyte was the 2.0 M KOH solution for electrochemical tests. In three-electrode measurements, the Co_3O_4/graphene hybrid fibers, Pt plate, and standard calomel electrode (SCE) were used as the working electrode, counter electrode, and reference electrode, respectively. The EIS was obtained under an ac voltage of 5 mV, frequency in the 10^6–0.01 Hz range, and open circuit. The specific capacitance (C_s) was calculated from the GCD curves,

$$C_s = \frac{I\Delta t}{m\Delta V} \quad (1)$$

where I, Δt, ΔV and m are the discharge current, discharge time, voltage range, and mass of the active materials on the electrodes, respectively.

Results and discussion

The morphologies of the RGO fibers and Co_3O_4/-graphene hybrid fibers were observed by SEM, as shown in Fig. 1. The RGO fibers contain the wrinkle overlapped GO nanosheets with a smooth surface. The diameter of the RGO fibers is around 48 μm (Fig. 1a). This type of wrinkle structure enlarges the specific surface area effectively, so it is able to enhance the transportation efficiency of electrolyte ion. Compared to the bare RGO fibers, SEM images of Co_3O_4/graphene hybrid fibers are very different (Fig. 1b–d). The diameter of the Co_3O_4/graphene hybrid fibers is around 69 μm (Fig. 1b). The Co_3O_4 with morphology of nanowires and nanosheets is formed on the surface of RGO fibers, leading to that the diameter evidently increases and the surface becomes slightly rough. The Co_3O_4 nanostructures directly grow from the surface of RGO fibers. This kind of specific nanostructure in fibers has never been reported before. Quite different from the previous studies that pseudocapacitive materials (e.g., MnO_2) were simply coated on the surface of RGO fibers without any nanotopography [27–29], the nanowires and nanosheets of Co_3O_4 nanostructure presented here display three-dimensional hierarchical structures and so have high specific surface area, having the ability to act as the active sites of redox reactions in full contact with the electrolyte, which may result in superior electrochemical properties compared with the solid nanoparticles. Figure 1e, f shows the EDS mapping images of the surface area of the Co_3O_4/graphene hybrid fibers. The images exhibit the presence of Co and O elements in the shell. The Co and O elements are uniformly distributed on the surface of the fibers, which confirms the Co_3O_4 grows homogeneously along the whole fiber. It is critical for improving the performances of supercapacitors based on the hybrid fibers.

Figure 2a shows Raman spectra of the RGO and Co_3O_4/graphene hybrid fibers. The peaks are found at around 1347.1 and 1586.6 cm^{-1} in both fibers, which are assigned to the defect induced D and G peaks, respectively. In addition, five new peaks appear at 186, 471, 513, 601, and 675 cm^{-1} for the Co_3O_4/graphene hybrid fibers, which are attributed to the F_{2g}, E_{2g}, F^1_{2g}, F^2_{2g}, and A^1_{1g} crystallization modes of Co_3O_4 crystal, respectively [30]. The observations reveal the formation of Co_3O_4 shell on the RGO core.

Figure 2b, c shows the core level XPS spectra of the Co_3O_4/graphene hybrid fibers. The C 1*s* spectra contain four peaks at 284.1, 285.6, 288.1, and 289.9 eV, which are ascribed to the C–C or C=C, C–O, C=O, and O–C=O bonds, respectively [31]. The observations indicate that the oxygen still exists in the graphene fibers. Note that the intensity of the oxygen-related peaks is rather low, suggesting the reduction in almost all GO. The Co 2*p* spectra contain two main components at 780.9 and 797.3 eV, which are assigned to the Co $2p_{3/2}$ and Co $2p_{1/2}$. They correspond to Co^{2+} and Co^{3+} in Co_3O_4, respectively, confirming that cobalt exists in the form of Co_3O_4. The two shake-up satellite peaks located around 786 and 803 eV are also characteristic of Co_3O_4, in good agreement with the former reports [30]. Now we can safely say that the observed results firmly confirm the successful growth of the Co_3O_4 nanostructures from the surface of the graphene fiber.

Figure 3a, b displays the photographs of the Co_3O_4/graphene fiber electrodes weaved into a textile and tied in a knot, which indicates the excellent flexibility and high strength of the hybrid fibers. The electrochemical properties of electrodes were studied by CV, GCD, and EIS measurements. As shown in Fig. 3c, the CV curves of Co_3O_4/graphene hybrid fiber electrodes show nearly rectangular shape, indicating a relatively good capacitive behavior under the 10–100 mV s^{-1} scan rates. Meanwhile, the

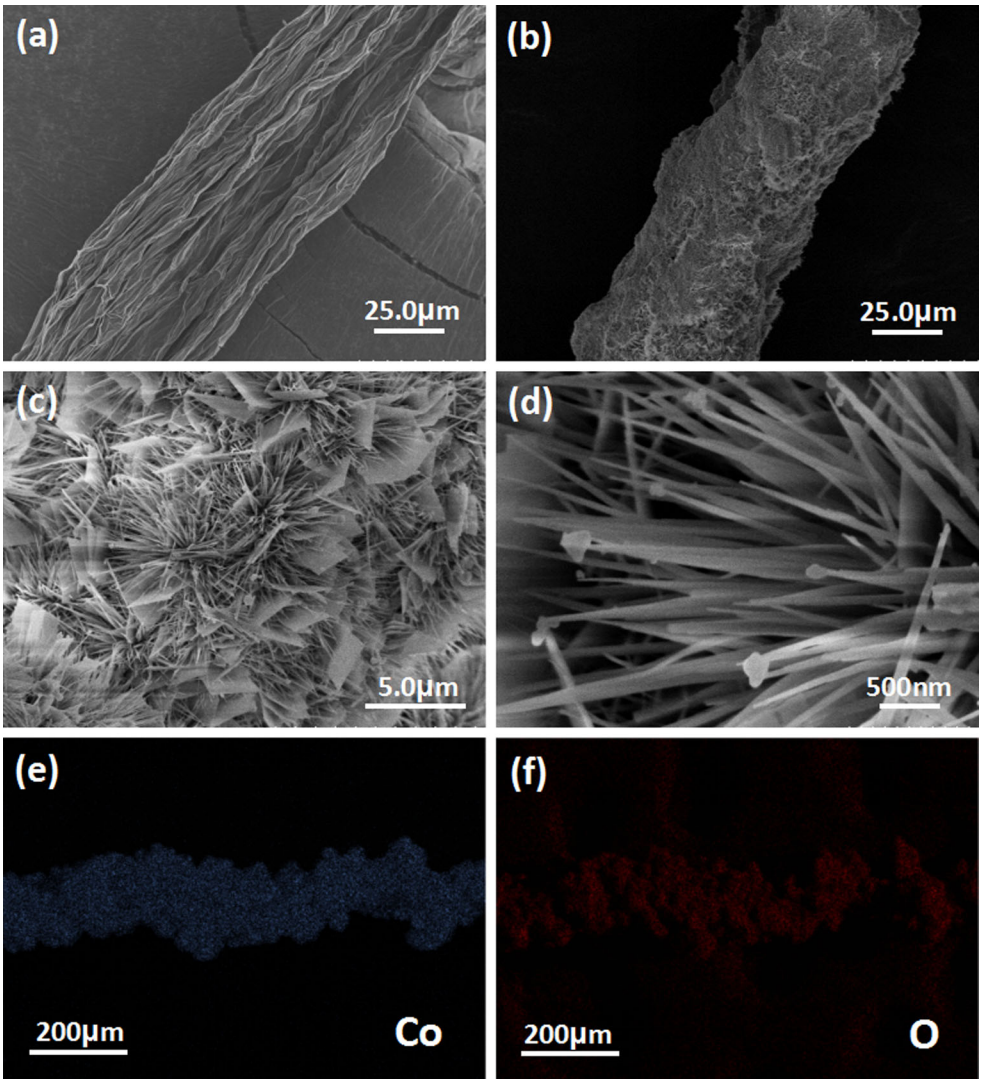

Figure 1 **a** SEM image of bare RGO fibers; **b** SEM image of Co_3O_4/graphene hybrid fibers; **c**, **d** SEM images of the surface of Co_3O_4/graphene hybrid fibers at different magnifications; **e**, **f** element mapping images of Co and O in Co_3O_4/graphene hybrid fibers.

CV curves show no evident faradaic current in the 0–0.8 V range, which demonstrates that the fiber electrodes are of ideal electrical double-layer capacitor behavior at the electrode/electrolyte interface. The highly conductive RGO fiber, combined with surface decorated Co_3O_4, is capable of accelerating ion transportation rate. It is seen that the current response displays the corresponding increases with the increase in the scan rate, exhibiting a good capacitive behavior of Co_3O_4/graphene hybrid fiber electrodes.

Figure 3d shows the Nyquist plots of the Co_3O_4/-graphene fiber electrodes. The curve displays an approximately vertical line, revealing the nature of capacitive behavior of the hybrid fiber electrodes [32]. The semicircle in the high frequency region is amplified in the set of Fig. 3d. The charge-transfer resistance (R_{ct}) is calculated by extrapolating the semicircle on the real axis. The charge-transfer resistances are 439 and 507 Ω for RGO fibers and Co_3O_4/graphene hybrid fibers electrodes, respectively. Moreover, the resistances of the electrochemical system (R_s) are 481 and 549 Ω for RGO fibers and Co_3O_4/graphene hybrid fibers electrodes, respectively. Note that the resistance ofCo_3O_4/graphene hybrid fibers is very close to that of RGO fibers, which is an encouraging result because there is no evident increase in resistance for RGO fibers with the formation of Co_3O_4 shell. The Co_3O_4 is of low electrical conductivity owing to its semiconductor

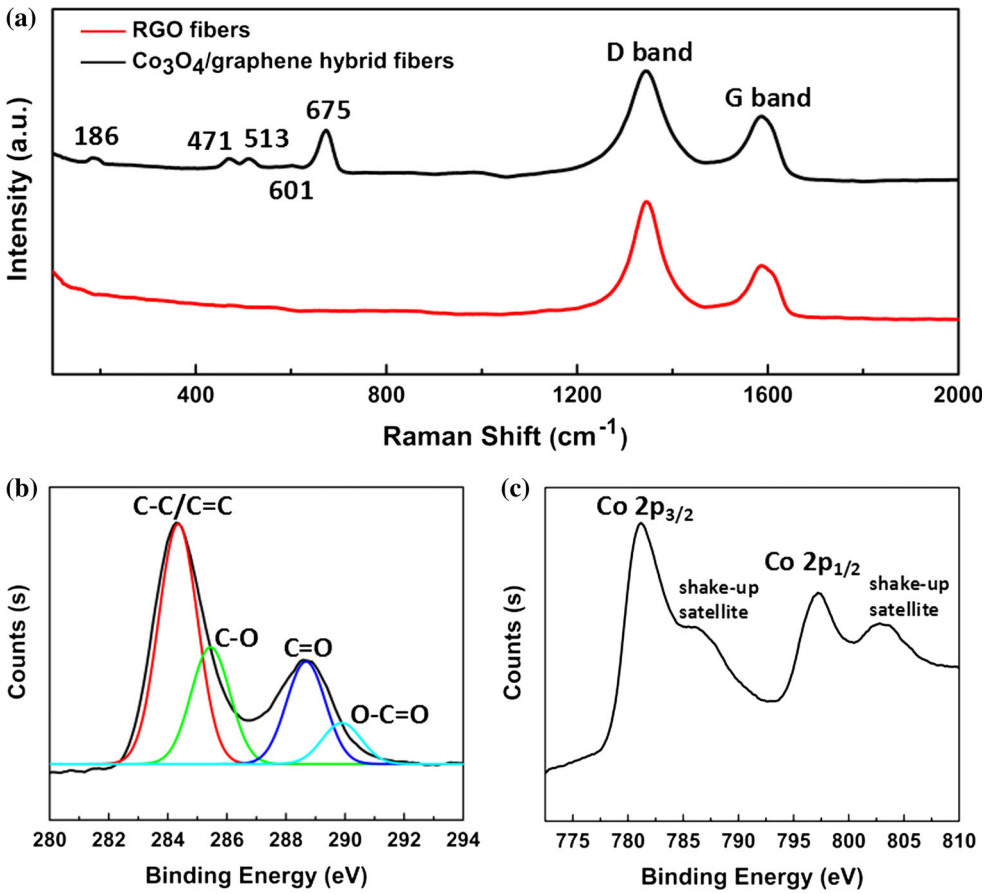

Figure 2 **a** Raman spectra of RGO and Co_3O_4/graphene hybrid fibers; **b**, **c** C 1*s* and Co 2*p* XPS core level spectra of Co_3O_4/graphene hybrid fibers.

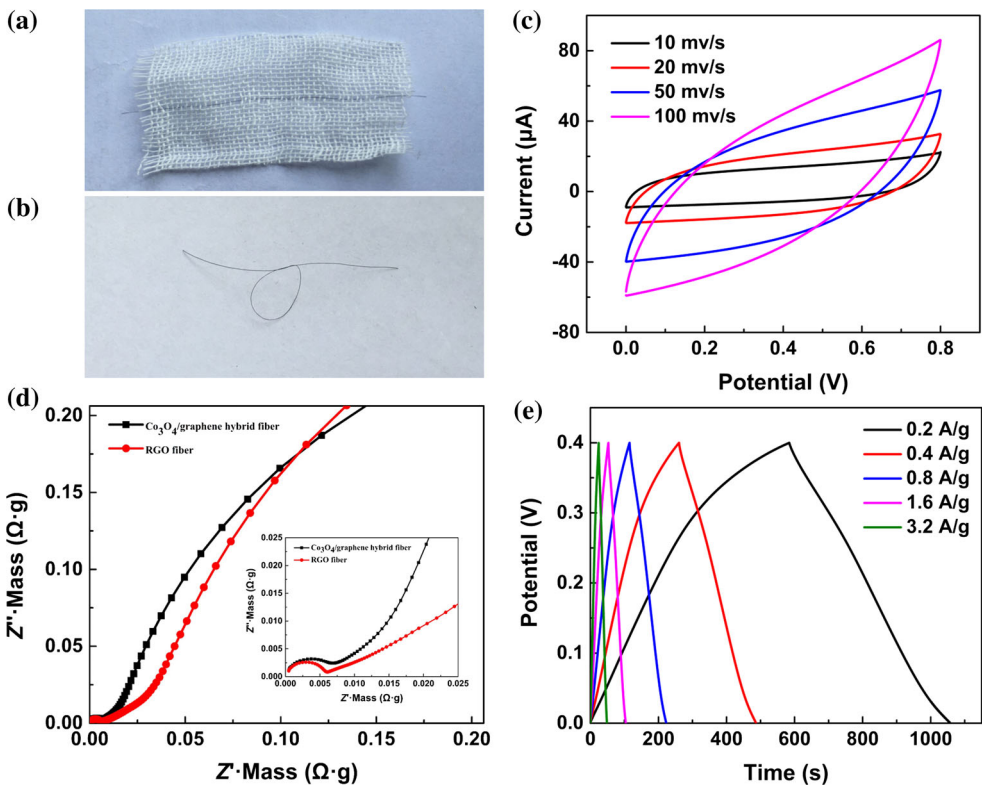

Figure 3 **a**, **b** Photographs of Co_3O_4/graphene hybrid fibers weaved into a textile and tied in a knot; **c** CV curves of Co_3O_4/graphene hybrid fibers at different scan rates; **d** EIS spectra of the RGO fibers and Co_3O_4/graphene hybrid fibers; **e** galvanostatic discharge voltage profiles of Co_3O_4/graphene hybrid fibers at various current densities.

characteristics. Compared with Co_3O_4, the observed data indicate that the electrical conductivity of Co_3O_4/graphene hybrid fiber electrodes is improved, which benefits from the highly conductive graphene. The effectively conductive links between Co_3O_4 and RGO fibers supply the rational paths for electrolyte ions, enhancing the electrical conductivity.

Figure 3e shows the GCD curves of the Co_3O_4/-graphene hybrid fiber electrodes at current densities from 0.2 to 3.2 A g^{-1}. All of the charging curves are symmetrical with their corresponding discharge counterparts, further indicating the ideal capacitive behavior of the electrodes. What is more, the GCD curves reveal excellent linear voltage–time appearances, suggesting the outstanding capacitive property of the hybrid fiber electrodes. Figure 4a shows the specific capacitance of the Co_3O_4/graphene hybrid fiber electrodes calculated from the GCD curves. At a current density of 0.2 A g^{-1}, the specific capacitance is up to 236.8 F g^{-1} (196.3 mF cm^{-2}, 165.7 F cm^{-3}). This high specific capacitance is clearly resulted from the large surface area of Co_3O_4 shell nanostructures serving as active sites of redox reactions. As the current density increases to 3.2 A g^{-1}, the specific capacitance of the Co_3O_4/-graphene hybrid fiber electrode is 192 F g^{-1}, retaining 81.1% of its value at 0.2 A g^{-1}, where the current density is elevated 16 times. The results reveal that the Co_3O_4/graphene hybrid fiber electrode has excellent rate capability, having great significance for energy storage devices. With increase in the current density, the gradual decrease in specific capacitance is attributed to the diffusion effect, which restricts the diffusion and migration of the electrolyte ions into the inside of electrodes at high current densities [33].

To investigate the cycle stability, the GCD tests were measured at 0.5 A g^{-1} for 10000 cycles, as shown in Fig. 4b. The 72.7% capacitance remained after 10000 cycles, revealing the outstanding long-term cycling stability. What is more, the GCD tests of the hybrid fibers after 1000 and 2000 times bending were measured at the same test conditions for 10000 cycles. Figure 4b shows the cycle stability remained almost unchanged after bending for 1000 and 2000 cycles, which indicated the hybrid fiber electrodes were highly flexible and their electrochemical performances could be well maintained under various deformations.

The RGO fibers electrode we prepared has also a considerable specific capacitance (67.5 F g^{-1}) at a current density of 1.0 A g^{-1}, as shown in Figure S1 (in Electronic Supporting Information). Compared with RGO fibers, the electrochemical performances of Co_3O_4/graphene hybrid fibers have been significantly improved through growing Co_3O_4 nanostructures on the surface of RGO fibers. Note that, the capacitance value of 236.8 F g^{-1} (196.3 mF cm^{-2}, 165.7 F cm^{-3}) of the Co_3O_4/graphene hybrid fibers are significantly higher than most of the graphene-based fiber electrodes previously reported, such as RGO–GO–RGO fibers (1.2 mF cm^{-2}) [3], PPy-decorated RGO/MWCNT fibers (25.9 F cm^{-3}) [34], graphene/polymer electrolyte coaxial fibers (182 F g^{-1}) [35], poly(vinyl alcohol)/graphene hybrid fibers (216 F g^{-1}) [36], and MnO_2-deposited graphene fibers (59.2 mF cm^{-2}) [29]. Details of the comparison are found in Table S1 (in Electronic Supporting Information), where all the available values for graphene-based fibers in previous reports are listed.

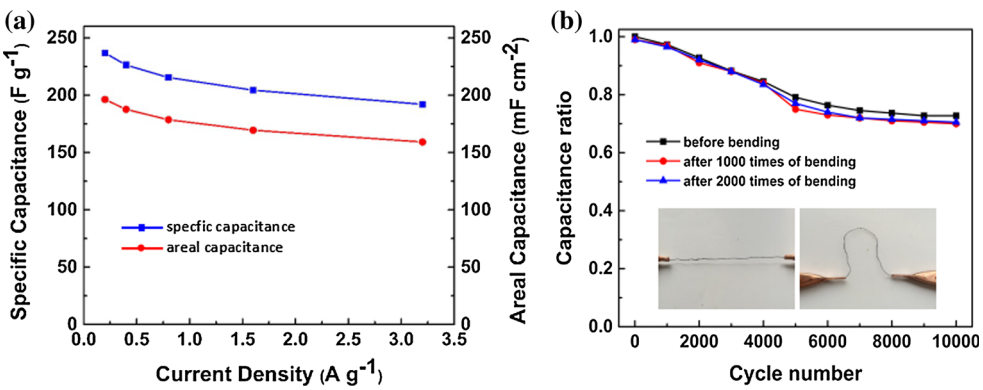

Figure 4 **a** Specific capacitance of Co_3O_4/graphene hybrid fibers at different current densities; **b** change of the capacitance ratio during the GCD cycling at 0.5 A g^{-1} before and after bending for 1000 and 2000 times.

Conclusions

In summary, a novel structure of Co_3O_4/graphene core–shell hybrid fibers has been developed by a hydrothermal method, exhibiting good flexibility and wearability with high electrochemical performances. The Co_3O_4 shell directly grows on the surface of the RGO fibers, forming 3D hierarchical morphology with double nanostructures of nanosheets and nanowires. The Co_3O_4/graphene hybrid fiber electrode shows a large specific capacitance of 236.8 F g^{-1} (196.3 mF cm^{-2}) at a current density of 0.2 A g^{-1} with superior rate capability. The capacitance retention is about 72.7% after 10000 cycles, having outstanding long-term cycling stability. By combination of the intrinsic mechanical flexibility of RGO core and the unique hierarchical structure with the pseudo-capacitance of Co_3O_4 shell, the Co_3O_4/-graphene hybrid fibers exhibit outstanding electrochemical capacitive behaviors with robust tolerance to mechanical deformation, very promising for wearable electronics.

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