Supporting Information

All-in-one Graphene-based Composite Fiber: Towards Wearable Supercapacitor

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Experimental Section

Materials

Graphite flakes, concentrated H_2SO_4 (98 %), H_3PO_4 , HCl, hydrogen iodide (HI) acid (40 %), Mn(CH₃COO)₂, P₂O₅, Poly(vinyl alcohol) (PVA), H_2O_2 (30% solution), $K_2S_2O_8$ and CaCl₂ were purchased from Sigma-Aldrich and used without further purification.

Preparation of GO suspensions

GO sheets were prepared from natural graphite flakes with an average lateral size of 200 μ m. The process included three steps: graphite expansion, graphite pre-oxididation, and graphite oxidation/exfoliation. In a typical process, 100 mL of 98% sulfuric acid and 35 mL of fuming nitric acid were gently poured into a 300 mL flask containing 3.5 g of natural graphite flakes. The as-prepared mixture was then vigorously stirred at room temperature for 24h. To dilute, after stirring, the black mixture was carefully poured into a beaker which contains 1.5 L of DDI water. Finally the black solid powder was collected by thorough washing and filtration of the mixture. The collected powder was then put in the oven at $60 \square$ overnight for thorough drying. The purpose of above procedure was to intercalate functional groups into packed graphite layers to facilitate the further thermal expansion. In a typical thermal expansion process, the obtained intercalated graphite powders were placed in the center of a quartz tube. The temperature of the tube furnace was then quickly increased to 950 \Box , and then the quartz tube was pushed into the furnace until the sample was located in the center of the heating zone for 12 seconds, after which the sample was pulled out again. It should be noted that the rapid increase of temperature will result in a dramatic volume expansion of the sample. The thermally expanded graphite powders were collected for a pre-oxidizing process. In this step, 200 mL of 98% sulfuric acid, 2.8 g K₂S₂O₈ and 4.2 g P₂O₅ were successively added into a 300 mL flask containing 3.5 g of asobtained thermally expanded graphite powders for vigorous stirring at 80 for 5 hours. After that, the mixture was cooled to room temperature and was then poured into a beaker with 1.5 L of DDI water . The diluted suspension was then filtered and washed repeatedly through a vacuum-filtration system utilizing a 0.2 μ m pore size polycarbonate membrane. The dark brown powders were collected and dried at 60 \Box in the oven overnight. Finally, an oxidation and exfoliation process was conducted to generate the GO suspension. In this process, the preoxidized graphite powders was slowly added to 150 mL of concentrated H₂SO₄ chilled to 0 \Box , then 12 g of KMnO₄ was slowly added into the suspension under gentle stirring. After stirring for 10 minutes, the temperature of the mixture was heated to 35 °C and was stirred for another 2 hours. 1.5 L of DDI water was then used to dilute the mixture followed by the slow addition of 7 mL of 30% hydrogen peroxide. The suspension was then left still for 48 hours until a clear supernatant was observed. Finally, the mixture was successively washed with DDI water, 1M HCl and DDI. The concentrated suspension was then collected and gently stirred. It should be noted that ultrasonication was avoided during these processes in order to prevent the large GO sheets from breaking to smaller ones.

Wet-Spinning for GO fibers and reducing to GF

The wet-spinning process was conducted on a lab-made spinning platform consisting of a mechanically propelled syringe and a controllable rotation plate. First, the coagulation bath was prepared by mixing ethanol and DDI water with a volume ratio of 1:3. CaCl₂ powders were then added into the mixture to form a 5% wt solution with vigorous stirring until completely dissolved. After securing the coagulation bath on the rotating plate, 6.5 mg mL⁻¹ of as-prepared GO suspension was injected into the coagulation bath with the rotation plate speed set to 25 rpm min⁻¹. A NE-1010 high pressure programmable single syringe pump was employed for extrusion of GO suspension with a 2.2 m min⁻¹ propulsion speed. The GO gel fibers can be continuously formed until the GO suspension in the syringe runs out. The GO fibers were immersed in the bottom of coagulation bath for 15 minutes to allow sufficient Ca²⁺ penetration for cross-linking

purpose. In order to remove the residual Ca^{2+} , the wet GO fibers were carefully transferred to DDI water for another 10 minutes. After that, the wet gel GO fibers were collected and dried for half an hour on a Teflon mounting bracket. Reduction of the fibers was performed using 30% wt HI acid heated to $80\Box$. The as-prepared GO fibers were then immersed into this HI acid solution for 10 minutes. Finally, the rGO fibers were collected and transferred to a bracket for later use.

Deposition of MnO₂

Hierarchical nanostructured MnO_2 was deposited onto the pristine backbone GF using an anodic electrodeposition method. To start, a 1 M manganese acetate solution was prepared by dissolving $Mn(CH_3COO)_2$ powder in DDI water with vigorous stirring until totally dissolved. Next, the deposition process was conducted in a three electrode system consisting of a working electrode (rGO fibers), a reference electrode (SCE electrode) and a counter electrode (carbon electrode). Before deposition, the pristine GF was immersed into the as-prepared electrolyte for 10 min for sufficient Mn^{2+} infiltration. A constant voltage of 1.2 V was applied for 5 minutes for continuous deposition. The thickness of MnO_2 layer was tunable by adjusting the deposition time.

Fabrication of AAGF, TGF and SGF devices

Procedure for making AAGF device is given in Fig 1. As described above, after deposition of MnO_2 , the GF@MnO₂ was immersed into the PVA/H₃PO₄ solution for 20 minutes in order to allow efficient coating. The gel electrolyte was prepared by dissolving 0.5 g PVA in 5 g DDI water with vigorous stirring under 80 \Box , followed by the addition of 0.4 g H₃PO₄ (80%) to make a homogenous mixture. GF@MnO₂ was then carefully separated from the gel solution after coating. After solidification, gel coated GF@MnO₂ was transferred to an 8 mg ml⁻¹ of GO suspension for outer sheath coating. After 8 minutes, the GO/gel/GF@MnO₂ was immersed into the ethanol/water/CaCl₂ coagulation bath for 1 minute for ionic crosslinking. Finally, the outside sheath of GO/gel/GF@MnO₂ was reduced in HI solution (30% in ethanol) at 80 \Box for 5 minutes. The use of ethanol as a reduction solvent can efficiently avoid re-dissolution of PVA above 80 \Box .

Fabrication of TGF was following the same procedure until deposition of MnO_2 . Then gel coated GF@MnO₂ and gel coated pristine GF were twisted into one fiber device as TGF. The same procedure for fabrication of AAGF was followed, while the SGF was prepared only without deposition of MnO₂.

Characterization

A powder diffractometer (MiniFlex 600, Rigaku) with a monochromatized CuK_a radiation source (λ = 0.154 178 nm) was employed for X-ray diffraction (XRD) studies in the 2 θ ranging from 5 to 90°. The Morphology characterization was performed by a LEO 1350 field emission scanning electron microscope (SEM) with an accelerating voltage of 5 kV. Raman spectra were obtained on a Senterra Raman detection system (Bruker Optics) using a 532 nm laser. XPS was carried out using a Thermo Scientific K-Alpha spectrometer system operated at 14.0 kV utilizing C 1s neutral carbon peak at 284.8 eV as reference.

Electrochemical studies were performed using a VMP3 potentiostat/galvanostat (Bio-Logic LLC, Knoxville, TN). Galvanostatic charge/discharge investigation was carried out by NEWARE BTS-CT3008 (Neware Technology, Ltd., Shenzhen, China). The total capacitance C=Q/ Δ V was evaluated by using half the integrated area of the CV curve to obtain the charge (Q), and subsequently dividing the charge by the width of the potential window (Δ V). The volume-normalized specific capacitance C_V=C/V (V=sample volume) and area-normalized specific capacitance Cs=C/S (S=sample area), calculated from the CV data, were investigated. Electrochemical impedance spectroscopy (EIS) and Galvanostatic charge–discharge studies were also carried out for further investigation.







Figure S2, real photo of (a) GOF, (b) pristine GF, (c) bundles knotted on a neat GF, (d-g) pristine GF bent to circle, hexagon, quadrilateral and triangle shapes without breaking, and (h) wrapped around a glass rod.



Fig. S3. SEM images of MnO₂ coated on GF in different magnifications (a-d)



Figure S4. SEM images of over mass loading deposition of MnO_2 on GF in different magnification (a-d). Bar scale is 10 μ m.



Figure S5. SEM images of (A), (B) TGF and (C), (D) AGF in different magnifications with corresponding schematic illustrations on the left



Figure S 6. Frequency dependence of (A) real capacitance and (B) imaginary capacitance for AAGF, SGF and TGF, respectively.



Figure S 7. Schematic illustration of AAGF devices integrating to non-woven fabric yarn