



Carbon Microfibers with Hierarchical Porous Structure from Electrospun Fiber-Like Natural Biopolymer

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SUBJECT AREAS:

SYNTHESIS AND
PROCESSING

POROUS MATERIALS

SUSTAINABILITY

BIOINSPIRED MATERIALS

Received

30 October 2012

Accepted

19 December 2012

Published

24 January 2013

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Electrospinning offers a powerful route for building one-dimensional (1D) micro/nanostructures, but a common requirement for toxic or corrosive organic solvents during the preparation of precursor solution has limited their large scale synthesis and broad applications. Here we report a facile and low-cost way to prepare 1D porous carbon microfibers by using an electrospun fiber-like natural product, i.e., silk cocoon, as precursor. We surprisingly found that by utilizing a simple carbonization treatment, the cocoon microfiber can be directly transformed into 1D carbon microfiber of ca. 6 μm diameter with a unique three-dimensional porous network structure composed of interconnected carbon nanoparticles of 10~40 nm diameter. We further showed that the as-prepared carbon product presents superior electrochemical performance as binder-free electrodes of supercapacitors and good adsorption property toward organic vapor.

Micro/nanomaterials have attracted great interest due to potential applications in adsorption, separation, catalysis, energy, sensors, nanoelectronic devices, biotechnology and other areas¹⁻⁸. Therefore, it is important to develop reliable methods for fabrication of micro/nanomaterials, with designed architecture as well as customized framework structure. Development of one-dimensional (1D) micro/nanomaterials has been one of the most active areas in the micro/nanomaterials science owing to their unique structure characteristics including high length/diameter ratio, large pore volume and high surface area⁹⁻¹⁷. Among such 1D micro/nanomaterials, porous carbon with 1D micro/nanostructure has attracted significant attention, not only for its fundamental scientific interest, but also for many modern-day technological applications^{9,18-23}. This was motivated by its unique physicochemical properties, i.e., good electrical conductivity, high surface area, and excellent chemical stability. A large number of advanced techniques have been developed to fabricate 1D porous carbonaceous nanostructure with well-controlled morphology and chemical composition. Generally, 1D micro/nanomaterials can be prepared by many methods including nanocasting, self-assembly, solvothermal synthesis and chemical vapor deposition^{12,15,19,24-26}. However, each of these methods has limitations, such as rigid reaction conditions, high cost, and complicated multiple synthetic steps.

Recently, electrospinning has been demonstrated to be a powerful technique to fabricate 1D micro/nanostructure. This method facilitates control over composition and topology of products, enabling enhanced performance in numerous applications^{18,27-29}. Despite rapid advances of electrospinning methodologies and their synthesis advantages (easiness, versatility, rapidity, etc.), current electrospinning procedures often involve toxic or corrosive organic solvents during the preparation of solution of starting materials, which is not in accordance with the urgent requirements of energy-saving and environmental protection. Hence, establishing an efficient and facile synthesis protocol using the precursors obtained directly from nature for preparation of 1D nanoporous carbons with well-tailored architectures would be of great benefit to their large scale production and broad applications.

In the present work, we report a facile and cost-effective way to prepare 1D porous carbon microfibers by using an electrospun fiber-like natural product, i.e., silk cocoon, as precursor. This biopolymer is obtained by a silkworm through an inartificial electrospinning-like process, in which the silkworm spins silk microfibers to form a cocoon around itself. We surprisingly found that by utilizing a simple carbonization treatment, the electrospun fiber-like natural cocoon microfibers can be directly transformed into 1D carbon microfibers with an average diameter of 6 μm (Figure 1). The 1D carbon microfibers consist of numerous carbon nanoparticle units of 10~40 nm in size, which are interconnected with each other to form a unique three-dimensional (3D) porous network structure. These carbon nanoparticle units are microporous, and their compact and loose

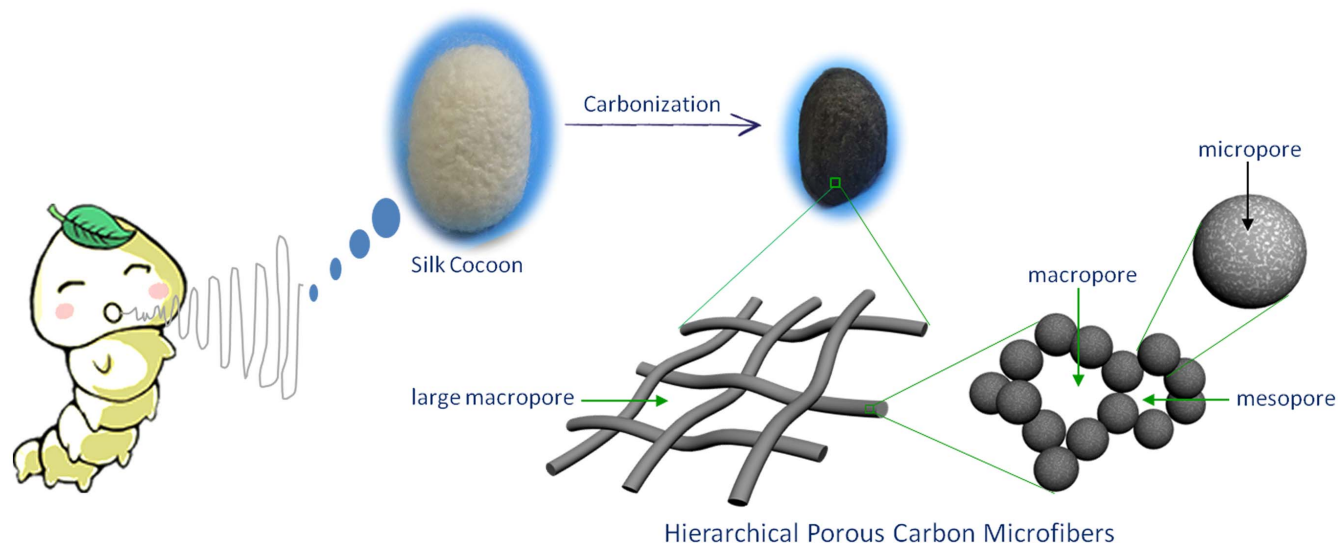


Figure 1 | Schematic illustration of the approach to fabricate hierarchical porous carbon microfibers from silk cocoon.

aggregation leads to mesopores and macropores, respectively. In the past, fabrication of porous network structures usually needed fussy and multiple synthetic steps including reaction-induced phase separation and supercritical drying¹⁴. Therefore, direct carbonization of such a natural biopolymer material without any additional harsh procedures makes the present approach more attractive in construction of micro/nanostructures. Furthermore, interlacement of these 1D carbon microfibers themselves in the carbonized cocoon leads to formation of large macropores.

Due to good pore interconnectivity, high surface area, large pore volume as well as high nitrogen content, the as-prepared 1D hierarchical porous carbon microfibers (HPCMF) show superior electrochemical performance as binder-free electrodes of supercapacitors and good adsorption property toward organic vapor. We hope that our present method will open up new avenues to advanced and sustainable materials, considering that the employment of low-cost and environment friendly silk cocoon as carbon source avoids many chemical reactions and physical processes in normal procedures for fabrication of 1D porous carbon fibers.

Results

SEM image in Figure S1A demonstrates that the silk cocoon is composed of interlaced 1D silk microfibers with about 15 μm in diameter. The silk microfibers are essentially nonporous, judging from their smooth framework surface (Figures S1B and S1C) as well as very low Brunauer–Emmett–Teller (BET) surface area of 7 m^2/g (Table S1). After a carbonization treatment at 900°C, the as-prepared carbon microfibers in the carbonized cocoon preserve the well-defined fibrous morphology (Figure 2A). The diameter of these carbon microfibers is measured to be about 6 μm , which is smaller than that of silk microfibers, indicating that the fibrous frameworks undergo an obvious shrinkage during carbonization because of burn-off of non-carbon elements and carbon-containing compounds. Surprisingly, it is obviously found from magnified SEM image of Figure 2B that the fibrous frameworks are uniformly fractured on the nanometer scale to form numerous interconnected carbon nanoparticles of 10~40 nm diameter during the high temperature pyrolysis treatment, although retaining the fibrous morphology (Figures 2A and 2C). As a result, the carbon microfibers obtained here have a unique hierarchical porous network structure: carbon nanoparticle units contain numerous micropores (see TEM image in Figure 2D), and their compact and loose aggregation leads to mesopores and macropores, respectively (Figure 2B).

Furthermore, interlacement of these 1D carbon microfibers themselves in the carbonized cocoon forms a great number of micron-scaled large macropores (Figure 2A).

N_2 adsorption method is used to further quantitatively elucidate the hierarchical porous structure of the as-obtained HPCMF. As shown in N_2 adsorption-desorption isotherm of Figure 3, the HPCMF has a high adsorption uptake at low relative pressure (P/P_0), indicative of the existence of plentiful micropores. In addition, the adsorption amount increases gradually and still does not reach a plateau near the P/P_0 of 1.0, demonstrating the presence of mesopores and macropores, which is in good agreement with the observation from SEM and TEM images. The pore size distribution (PSD) curve obtained using density functional theory (DFT) is displayed in Figure 3. Three regions can be confirmed: (1) micropores (<2 nm) with a PSD peak at 1.3 nm; (2) mesopores (2~50 nm) with a

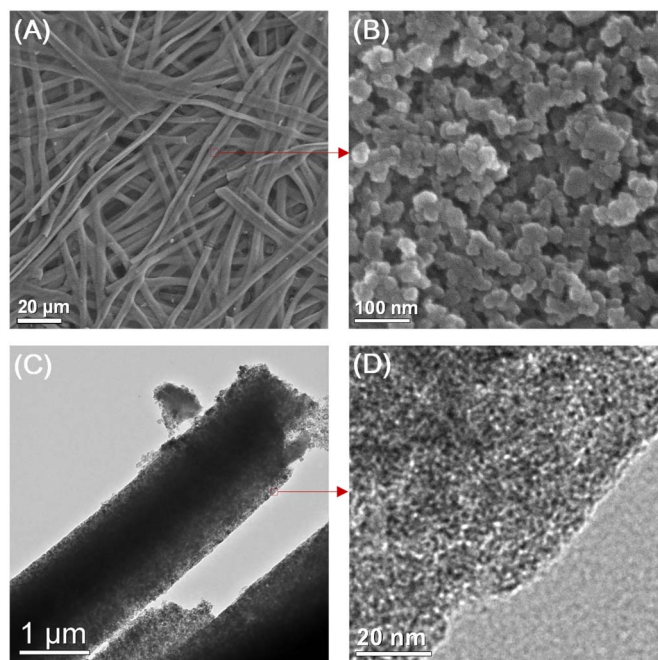


Figure 2 | (A, B) SEM and (C, D) TEM images of HPCMF. (B) and (D) correspond to the area indicated by a rectangle in (A) and (C), respectively.

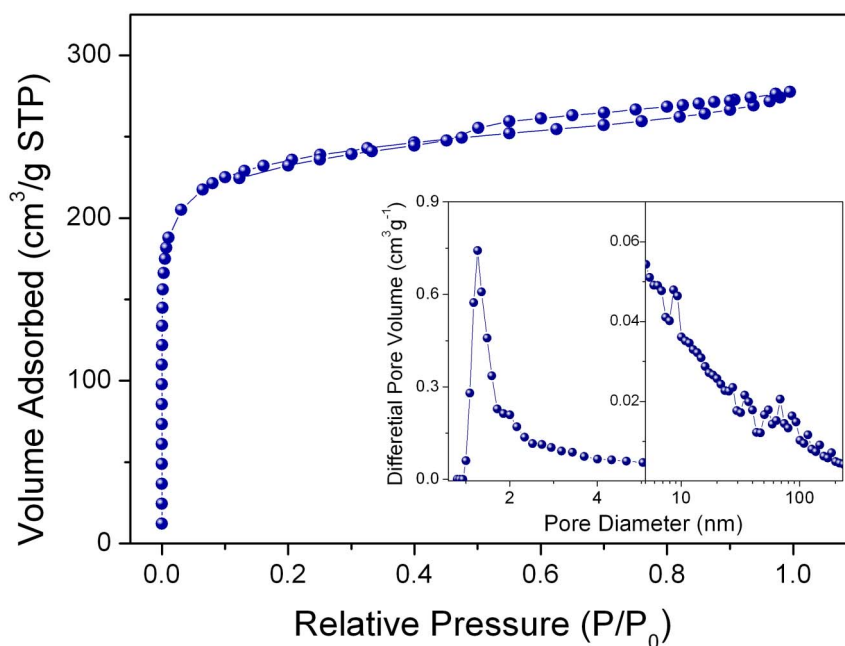


Figure 3 | N_2 adsorption-desorption isotherm of HPCMF. The inset shows its DFT pore size distribution.

maximum PSD peak at 9 nm; and (3) macropores (50~400 nm) with a maximum PSD peak at 68 nm. It should be noted that large macropores, i.e., the spaces between interlaced 1D carbon fibers and between very loosely aggregated carbon nanoparticles may be too large and too open to lead to capillary condensation and thus to be reflected in pore size distribution. As shown in Table S1, a BET calculation gives the BET surface area for the HPCMF equal to $796 \text{ m}^2/\text{g}$; and the t-plot method gives the surface areas of micropores and external large-sized pores equal to 569 and $227 \text{ m}^2/\text{g}$, respectively. Moreover, the total pore volume is calculated to be $0.43 \text{ cm}^3/\text{g}$ according to the amount adsorbed at a relative pressure P/P_0 of 0.99 .

The HPCMF from silk cocoon is found to have nitrogen-containing functional groups by means of the combustion analysis, X-ray photoelectron spectroscopy (XPS) and electron energy loss spectroscopy (EELS). The nitrogen content, as measured by the combustion analysis, is about $6.5 \text{ wt.}\%$ (Table S1), and $4.5 \text{ at.}\%$, according to XPS (Table S2). The nitrogen element is distributed homogeneously within the carbon framework of HPCMF, according to EELS mapping images of carbon and nitrogen elements (Figure 4). The nitrogen-containing functional groups are determined by the deconvolution of high resolution N 1s XPS spectrum (Figure S2). As schematically illustrated in Figure S3, the N 1s spectrum can be

deconvoluted into four functional components³⁰, i.e., pyridinic N (N-6), quaternary N (N-Q), pyrrolic N (N-5), and pyridine-N-oxide (N-X), whose percentage is $23.9 \text{ at.}\%$, $24.6 \text{ at.}\%$, $47.7 \text{ at.}\%$ and $3.8 \text{ at.}\%$, respectively (Table S2).

Besides the above unique hierarchical structure, another important characteristic of HPCMF is its stable, regulable and versatile bulk form. Figures 5A and 5B display the photographs of a silk cocoon before and after carbonization. It can be found that the elliptical shape of cocoon is well retained after pyrolysis, although its color turns from white to black because of carbonization. The carbonized cocoon is easily tailored into various forms, e.g., rectangle felt (Figure S4).

In this study, to test its feasibility for practical application, the silk cocoon-based HPCMF in the form of rectangle felt is directly used as a binder-free electrode for supercapacitor without any fussy electrode preparation processes which are necessary for normal production of carbon electrodes. The supercapacitor device is assembled by attaching two pieces of HPCMF felts that are immersed in a small seal bag containing 6 mol/L KOH aqueous electrolytes, as shown in Figure 5C. It is shown that the HPCMF has good capacitive performance (Figures 5D and S5). For example, at the sweep rate of 2 mV/s , HPCMF possesses a mass specific capacitance as high as 215 F/g , which translates into a capacitance per surface area up to $27 \text{ }\mu\text{F}/\text{cm}^2$,

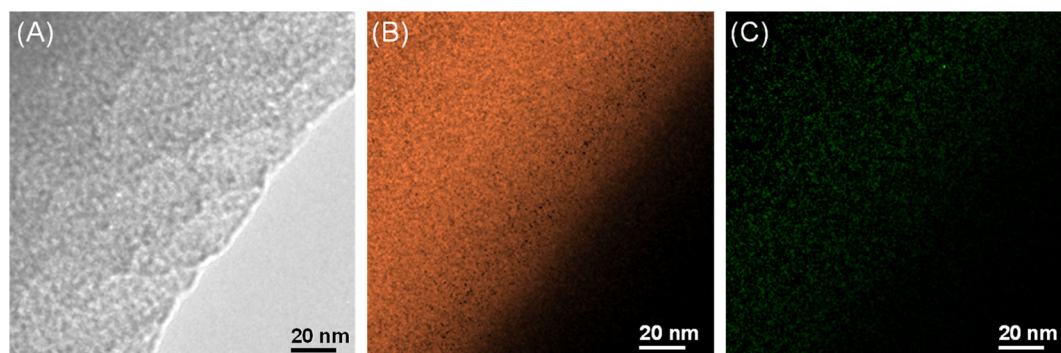


Figure 4 | EELS mapping images of HPCMF: (A) bright-field image, (B) carbon and (C) nitrogen.

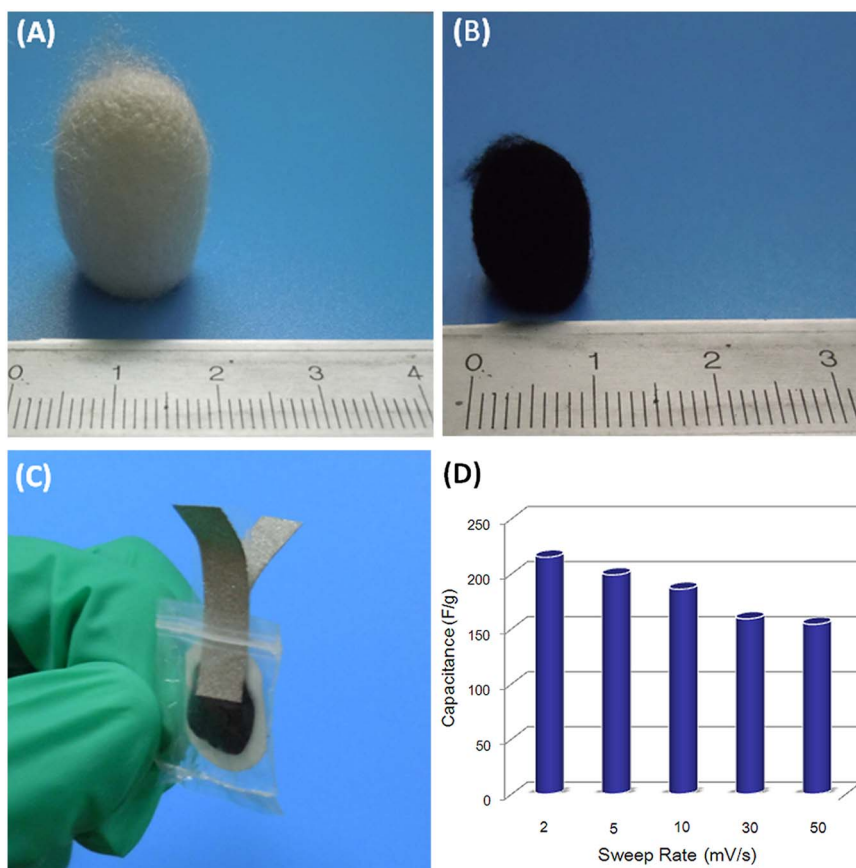


Figure 5 | Photographs of a silk cocoon before (A) and after (B) carbonization, (C) the as-fabricated binder-free HPCMF based supercapacitor, and (D) specific capacitances at various sweep rates for binder-free HPCMF based electrodes.

a value higher than those of most porous carbons³¹. With further increasing the sweep rate to 50 mV/s, a high mass specific capacitance (154 F/g) is still observed, indicative of excellent rate capability in HPCMF electrodes. The good capacitive performance of HPCMF may arise from its unique hierarchical pore structure that is beneficial to ionic transportation and storage. The interpenetrated fiber network texture combined with the hierarchical nanoporous structure in the carbon fiber framework ensures quick penetration of electrolytes, thus reducing the resistance for the ions^{32–34}. Moreover, it is believed that the plentiful nitrogen functional groups in the carbon framework can not only improve the wettability of the as-prepared material in the electrolyte but also provide great pseudocapacitance^{35,36}.

Another potential use of the HPCMF is explored for adsorption toward organic vapor. As shown in adsorption isotherm of methanol vapor for HPCMF in Figure S6, HPCMF exhibits an uptake in the range of low relative pressures, because of the presence of numerous micropores. With increasing the relative pressure, the adsorption capacity continuously increases because of condensation of methanol in mesopores and macropores. Therefore, HPCMF gives the adsorption capacity of methanol as high as 243 mg/g.

Discussion

We have successfully fabricated a class of novel 1D HPCMF using a simple one-step carbonization of electrospun fiber-like natural biopolymer, i.e., silk cocoon. As one of the most abundant types of natural biomass, silk cocoon can be produced via an inartificial electrospinning-like process. After carbonization, the silk microfibers can be directly transformed into 1D carbon microfibers of *ca.* 6 μm diameter with a unique hierarchical porous structure composed of interconnected carbon nanoparticles of 10–40 nm

diameter and a high surface area of *ca.* 800 m^2/g . It is worth mentioning that the employment of natural silk cocoon as carbon source helps to avoid many chemical reactions and physical processes in normal synthetic procedures of 1D porous carbon fibers, such as preparation of carbon sources and templates, utilization of abundant hazardous organic solution during electrospinning process, and/or subsequent template removal. Furthermore, the combination of 1D fibrous morphology, hierarchical porous network structure and good pore interconnectivity facilitates easy access of reaction species to the inner surface of carbon fiber, and these small-sized nanopores effectively increase the surface area available for active site dispersion, which is very helpful in many applications.

On the other hand, this natural biopolymer silk cocoon is composed of fibroin (72–81%), sericin (19–28%) and very little other materials such as fats, wax, sand pigments plus minerals. As shown in Table S1, silk cocoon contains considerable nitrogen atoms (16.2 wt.%), because its chemical structure is mainly characterized by the presence of 18 types of amino acids such as glycine, alanine and serine. Therefore, it is not surprising that the HPCMF materials contain a certain amount of nitrogen-containing functional groups. It is expected that the introduction of these nitrogen-containing functional groups can not only boost the material performance, e.g., in the case of energy storage or catalysis, but also completely change the electronic properties that are attractive for a wide variety of applications³⁷.

In addition, the tailorable bulk form of HPCMF is also a valuable characteristic, which is derived from good shape stability of silk cocoon during carbonization. This feature provides an opportunity to control the bulk form to cater to the need of any targeted application.

Due to these excellent physical and chemical advantages discussed above, the HPCMF materials have been proven to present great



potential for use as binder-free electrodes for supercapacitor devices (e.g., a capacitance as high as 215 F/g) and as an adsorbent toward organic vapors like methanol (e.g., an adsorption capacity up to 243 mg/g). We hope that our finding will provide a new benchmark for fabricating sustainable materials with advanced micro/nanostructure, given that the huge amount of silk cocoon is produced and its related carbon material can be prepared facilely at low cost.

Methods

Bombyx mori silk cocoon was directly used as the starting material without any pretreatment. The silk cocoon was subjected to carbonization by heating at 900 °C for 3 h under N₂ flow. The heating rate was 2 °C/min.

The microstructure of the samples was investigated by a JSM-6330F scanning electron microscope (SEM) and JEM-2010HR transmission electron microscope (TEM). EELS mapping images were obtained by a FEI F30 TEM. Elemental analysis was performed on an Elementar Analysensysteme GmbH Vario EL analyzer. XPS measurement was accomplished using an ESCALAB250 instrument. N₂ adsorption measurement was carried out using a Micromeritics ASAP 2010 analyzer at 77 K. The BET surface area (S_{BET}) was analyzed by Brunauer–Emmett–Teller (BET) theory. The total pore volume (V_t) was estimated from the amount adsorbed at a relative pressure P/P_0 of 0.99. The external surface area (S_{ext}) and micropore surface area (S_{mic}) was determined by t-plot theory. The pore size distribution was analyzed by original density functional theory (DFT) combined with non-negative regularization and medium smoothing.

The binder-free electrodes were directly obtained from the carbonized silk cocoon which was cut into the form of rectangle felt before carbonization. The simple supercapacitor device was fabricated by attaching two pieces of HPCMF felt electrodes with the same mass that were immersed in a small seal bag containing 6 mol/L KOH aqueous solution. A piece of polypropylene-based non-woven fabric as a separator was placed between the HPCMF felt electrodes and two nickel foams were inserted onto the edge of the electrodes in order to connect the electrochemical test instruments. The electrochemical measurements were carried out using an IM6e electrochemical workstation. The specific capacitance (C_m) was calculated according to the equation $C_m = \frac{2I}{v \cdot m}$, where I , v and m represent the current at the middle voltage of the potential window, the sweep rate and the mass of single HPCMF felt electrode, respectively. The adsorption measurement toward methanol vapor was carried out at 25 °C by using an IG-3 intelligent gravimetric analyzer (Hidden Isochema, Ltd., Warrington, UK).

- Seo, M. & Hillmyer, M. A. Reticulated Nanoporous Polymers by Controlled Polymerization-Induced Microphase Separation. *Science* **336**, 1422–1425 (2012).
- Joo, S. H. *et al.* Ordered nanoporous arrays of carbon supporting high dispersions of platinum nanoparticles. *Nature* **412**, 169–172 (2001).
- Liu, C., Li, F., Ma, L. P. & Cheng, H. M. Advanced Materials for Energy Storage. *Adv. Mater.* **22**, E28–E62 (2010).
- Brezesinski, T., Wang, J., Tolbert, S. H. & Dunn, B. Ordered mesoporous alpha-MoO₃ with iso-oriented nanocrystalline walls for thin-film pseudocapacitors. *Nat. Mater.* **9**, 146–151 (2010).
- Tang, C. *et al.* Nanoporous carbon films from "hairy" polyacrylonitrile-grafted colloidal silica nanoparticles. *Adv. Mater.* **20**, 1516–1522 (2008).
- Choi, M. & Ryoo, R. Ordered nanoporous polymer-carbon composites. *Nat. Mater.* **2**, 473–476 (2003).
- Zhu, Y. *et al.* Carbon-based supercapacitors produced by activation of graphene. *Science* **332**, 1537–1541 (2011).
- Nagai, A. *et al.* Pore surface engineering in covalent organic frameworks. *Nat. Commun.* **2**, 536–544 (2011).
- Zhang, J. *et al.* Surface-modified carbon nanotubes catalyze oxidative dehydrogenation of n-butane. *Science* **322**, 73–77 (2008).
- Lu, X. F., Wang, C. & Wei, Y. One-Dimensional Composite Nanomaterials: Synthesis by Electrospinning and Their Applications. *Small* **5**, 2349–2370 (2009).
- Bourret, G. R. & Lennox, R. B. 1D Cu(OH)(2) Nanomaterial Synthesis Templated in Water Microdroplets. *J. Am. Chem. Soc.* **132**, 6657–6659 (2010).
- Hartergerink, J. D., Beniash, E. & Stupp, S. I. Self-assembly and mineralization of peptide-amphiphile nanofibers. *Science* **294**, 1684–1688 (2001).
- Su, D. S. & Schlögl, R. Nanostructured Carbon and Carbon Nanocomposites for Electrochemical Energy Storage Applications. *ChemSuschem* **3**, 136–168 (2010).
- Wu, D. *et al.* Design and Preparation of Porous Polymers. *Chem. Rev.* **112**, 3959–4015 (2012).
- Dong, Z. X., Kennedy, S. J. & Wu, Y. Q. Electrospinning materials for energy-related applications and devices. *J. Power Sources* **196**, 4886–4904 (2011).
- Wu, D. *et al.* Preparation of Polymeric Nanoscale Networks from Cylindrical Molecular Bottlebrushes. *ACS Nano* **6**, 6208–6214 (2012).
- Su, D. S. The Use of Natural Materials in Nanocarbon Synthesis. *ChemSuschem* **2**, 1009–1020 (2009).
- Inagaki, M., Yang, Y. & Kang, F. Carbon nanofibers prepared via electrospinning. *Adv. Mater.* **24**, 2547–2566 (2012).
- Li, W. *et al.* A Self-Template Strategy for the Synthesis of Mesoporous Carbon Nanofibers as Advanced Supercapacitor Electrodes. *Adv. Energy Mater.* **1**, 382–386 (2011).
- Hunt, M. A., Saito, T., Brown, R. H., Kumbhar, A. S. & Naskar, A. K. Patterned functional carbon fibers from polyethylene. *Adv. Mater.* **24**, 2386–2389 (2012).
- Su, D. S. *et al.* Hierarchically structured carbon: Synthesis of carbon nanofibers nested inside or immobilized onto modified activated carbon. *Angew. Chem. Int. Ed.* **44**, 5488–5492 (2005).
- Yang, Q. H., Xu, W. H., Tomita, A. & Kyotani, T. The template synthesis of double coaxial carbon nanotubes with nitrogen-doped and boron-doped multiwalls. *J. Am. Chem. Soc.* **127**, 8956–8957 (2005).
- Lv, R. T. *et al.* Open-Ended, N-Doped Carbon Nanotube-Graphene Hybrid Nanostructures as High-Performance Catalyst Support. *Adv. Funct. Mater.* **21**, 999–1006 (2011).
- Su, D. S. *et al.* Mount-Etna-Lava-Supported Nanocarbons for Oxidative Dehydrogenation Reactions. *Adv. Mater.* **20**, 3597–3600 (2008).
- Chen, J. T., Chen, W. L. & Fan, P. W. Hierarchical Structures by Wetting Porous Templates with Electrospun Polymer Fibers. *ACS Macro Lett.* **1**, 41–46 (2011).
- Wang, X. & Li, Y. Selected-Control Hydrothermal Synthesis of α - and β -MnO₂ Single Crystal Nanowires. *J. Am. Chem. Soc.* **124**, 2880–2881 (2002).
- Cavaliere, S., Subianto, S., Savych, I., Jones, D. J. & Roziere, J. Electrospinning: designed architectures for energy conversion and storage devices. *Energy Environ. Sci.* **4**, 4761–4785 (2011).
- Chen, Y. M., Lu, Z. G., Zhou, L. M., Mai, Y. W. & Huang, H. T. Triple-coaxial electrospun amorphous carbon nanotubes with hollow graphitic carbon nanospheres for high-performance Li ion batteries. *Energy Environ. Sci.* **5**, 7898–7902 (2012).
- Tsaroam, A., Matyjaszewski, K. & Silverstein, M. S. Spontaneous core-sheath formation in electrospun nanofibers. *Polymer* **52**, 2869–2876 (2011).
- Hulicova-Jurcakova, D., Sereych, M., Lu, G. Q. & Bandosz, T. J. Combined Effect of Nitrogen- and Oxygen-Containing Functional Groups of Microporous Activated Carbon on its Electrochemical Performance in Supercapacitors. *Adv. Funct. Mater.* **19**, 438–447 (2009).
- Huang, C. H. *et al.* Three-dimensional hierarchically ordered porous carbons with partially graphitic nanostructures for electrochemical capacitive energy storage. *ChemSuschem* **5**, 563–571 (2012).
- El-Kady, M. F., Strong, V., Dubin, S. & Kaner, R. B. Laser scribing of high-performance and flexible graphene-based electrochemical capacitors. *Science* **335**, 1326–1330 (2012).
- Liang, Y., Wu, D. & Fu, R. Preparation and electrochemical performance of novel ordered mesoporous carbon with an interconnected channel structure. *Langmuir* **25**, 7783–7785 (2009).
- Wang, D. W., Li, F., Liu, M., Lu, G. Q. & Cheng, H. M. 3D aperiodic hierarchical porous graphitic carbon material for high-rate electrochemical capacitive energy storage. *Angew. Chem. Int. Ed.* **47**, 373–376 (2008).
- Yang, X., Wu, D., Chen, X. & Fu, R. Nitrogen-Enriched Nanocarbons with a 3-D Continuous Mesopore Structure from Polyacrylonitrile for Supercapacitor Application. *J. Phys. Chem. C* **114**, 8581–8586 (2010).
- Simon, P. & Gogotsi, Y. Materials for electrochemical capacitors. *Nat. Mater.* **7**, 845–854 (2008).
- Mane, G. P. *et al.* Preparation of Highly Ordered Nitrogen-Containing Mesoporous Carbon from a Gelatin Biomolecule and its Excellent Sensing of Acetic Acid. *Adv. Funct. Mater.* **22**, 3596–3604 (2012).

Acknowledgements

This research was supported by the project of NNSFC (51173213, 51172290, 51232005, 50802116), Program for New Century Excellent Talents in University, Program for Pearl River New Star of Science and Technology in Guangzhou, the Fundamental Research Funds for the Central Universities (09lgpy18), and the Project of Demonstration Base of Department of Education of Guangdong Province (cghzd0901). Mr. Chaolun Liang (Instrumental Analysis & Research Center, Sun Yat-sen University) is acknowledged for help with EELS measurements.

Author contributions

D.W. conceived the project. Y.L. conducted the experiments. All the authors discussed the results. Y.L. and D.W. wrote the manuscript.

Additional information

Supplementary information accompanies this paper at <http://www.nature.com/scientificreports>

Competing financial interests: The authors declare no competing financial interests.

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How to cite this article: Liang, Y., Wu, D. & Fu, R. Carbon Microfibers with Hierarchical Porous Structure from Electrospun Fiber-Like Natural Biopolymer. *Sci. Rep.* **3**, 1119; DOI:10.1038/srep01119 (2013).