Supporting Information for

Flexible Heteroatom-doped Graphitic Hollow Carbon Fibers for Ultrasensitive and Reusable Electric Current Sensing

Zhiping Jiang, Yue Shao, Peng Zhao, and Hong Wang*

Key Laboratory of Functional Polymer Materials of Ministry of Education, Institute of Polymer Chemistry, College of Chemistry, Nankai University, Tianjin 300071, P.R. China;

Corresponding author: hongwang1104@nankai.edu.cn

Experimental

Materials

The “Human hairs” were collected from a healthy Chinese volunteer in Nankai University. “Rabbit hairs” and wools were collected from market at Lanzhou city located at northwest in China. All of the “hairs” were carefully rinsed thoroughly with DI water, acetone and ethanol three times (each time for 30 min) in order to remove dust and adhering grease before usage. 10,12-Pentacosadiynoic acid was purchased from Sigma-Aldrich (≥97.0%) and were filtered using the membrane with the pore diameter of 20 nm to remove any PDA present prior to use Ethanol, acetone and tetrahydrofuran were of analytic grade. The vacuum oil pump (model 2XZ-4) is purchased from Qiujing Vacuum Pump Co. Ltd. and the vacuum pressure is 6×10^{-2} Pa.

Preparation of CFs

All of the “hairs” were carefully rinsed thoroughly with DI water, acetone and ethanol three times (each time for 30 min) in order to remove dust and adhering grease before usage. In typical carbonization procedures, the thoroughly washed “hairs” were placed in a small crucible and carbonized at 1000 °C for 2 hours under vacuum to afford CFs.

Preparation of PDA/CFs

The purified 10,12-Pentacosadiynoic acid was firstly dissolved in tetrahydrofuran with a concentration of 30 mg ml^{-1}. A single CF was dipped into the precursor solution, followed by evaporation of solvent at room temperature. Before polymerization, the treated CFs were exposed to the open air in a hood for 24 h. Then, 10,12-Pentacosadiynoic acid was polymerized at room temperature under UV light with a wavelength of 254 nm for 2 h.

Characterization and Measurements

X-ray diffraction was obtained on Rigaku MiniFlex600 (Cu Kα radiation). The morphology of different carbon fibers was viewed by field-emission scanning electron microscopy (SEM, JEOL JSM7500F). Transmission electron microscopy and high-resolution transmission electron microscopy images (TEM and HRTE) were measured by a Philips Tecnai G2F-20 with

acceleration voltage of 200 kV and equipped with electron energy loss spectroscopy. The thermogravimetric analysis (TGA) was carried out on a NETZSCH STA 409PC instrument under purified nitrogen gas flow at 10°C min^{-1}. Elemental analyses were obtained from the service of Mikroanalytisches Labor Pascher (Remagen, Germany). XPS data was collected by an Axis Ultra instrument (Kratos Analytical) under ultrahigh vacuum (<10^{-8} Torr) and by using a monochromatic Al Ka X-ray source. The adventitious carbon 1 s peak was calibrated at 285 eV and used as an internal standard to compensate for any charging effects. Raman measurements were performed on a Renishaw inVia Reflex with an excitation wavelength of 473nm and laser power of 100 mW at room temperature. The electric conductivity of CFs was measured by recording I–V curves with a Keithley 4200A Source. The DC power supply was used to generate direct current (model GPS-605D, from Shenzhen Guce Electronics Co., Ltd); The alternating current was generated by NAPUI PW-500 AC variable frequency power supply.

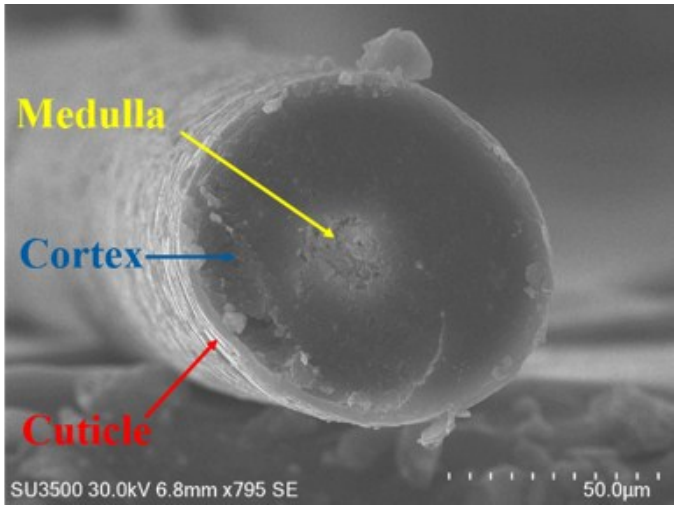

Figure S1. Cross-section SEM image of "human hair".

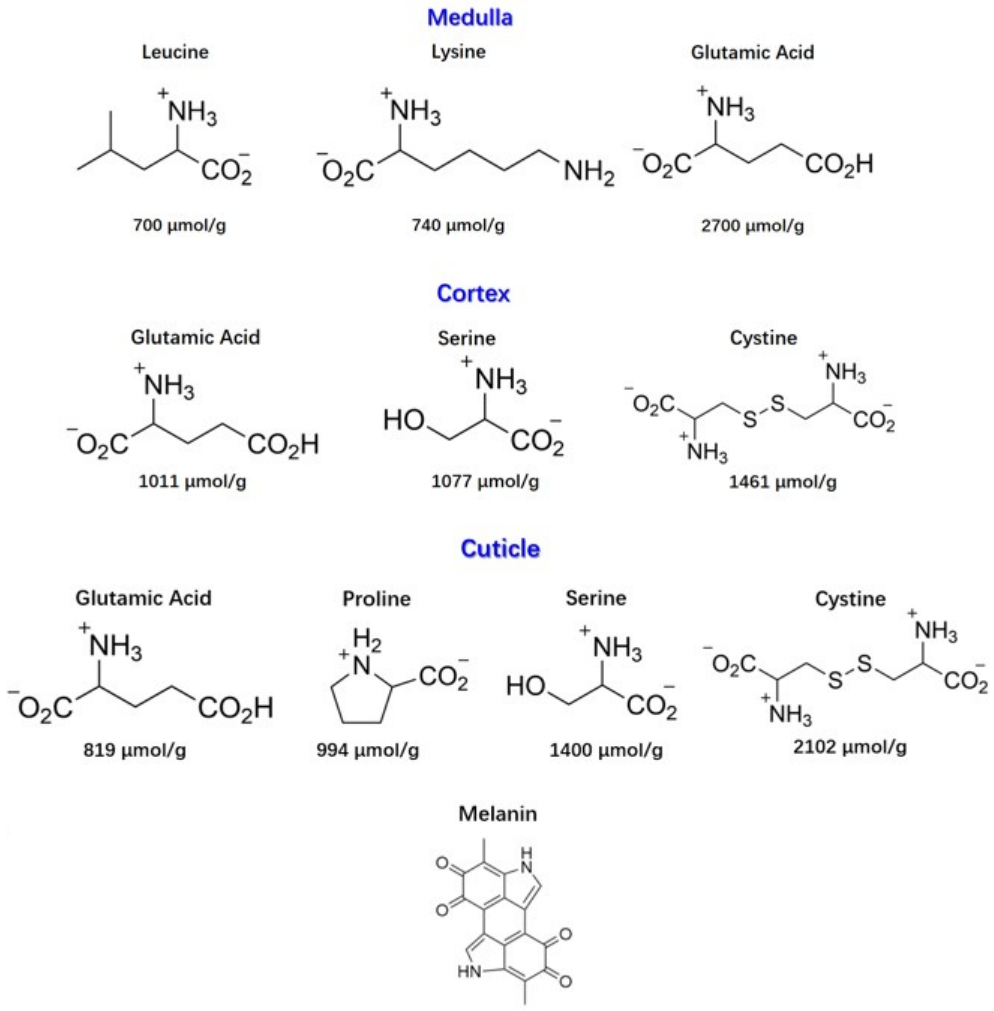

Figure S2. The chemical structures of most amino acids found in hydrolyzates form and pigment in Medulla, Cortex and Cuticle. Data are expressed in micromoles amino acid per gram dry hair[S1].

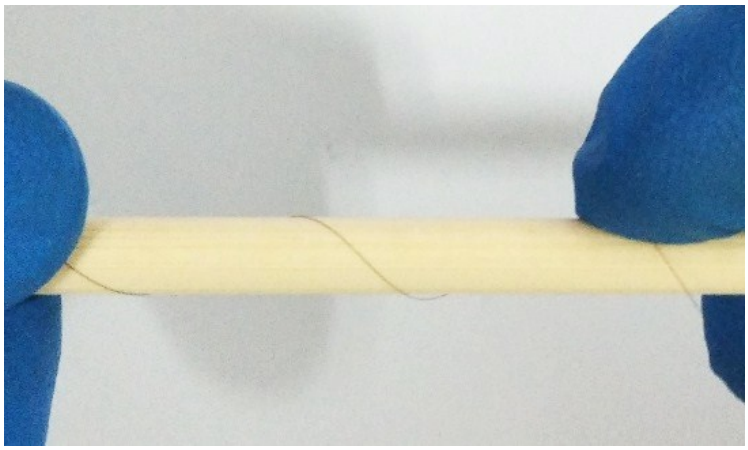

Figure S3. Digital photograph of a CF wrapped on a chopstick.

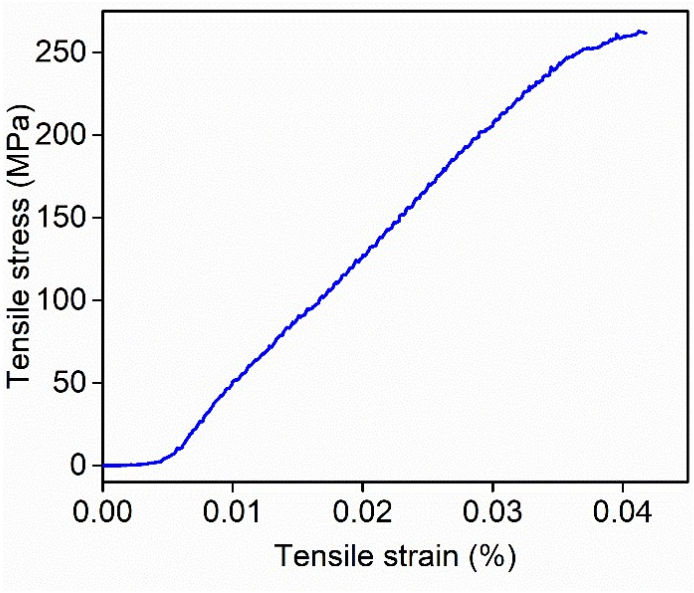

Figure S4. Tensile stress-strain curve of a CF.

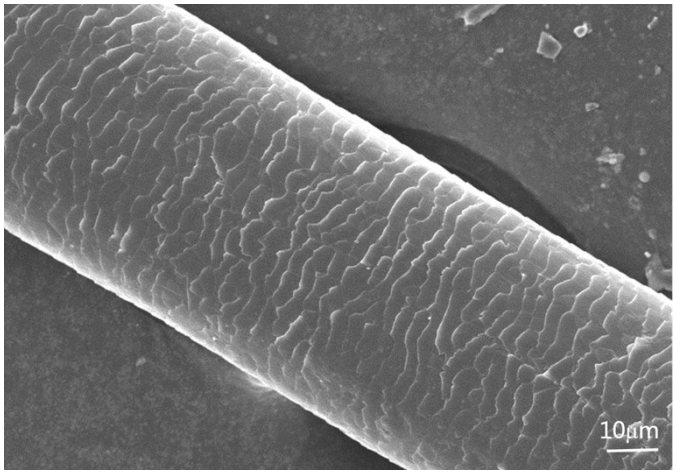

Figure S5. Representative surface SEM image of “human hairs”.

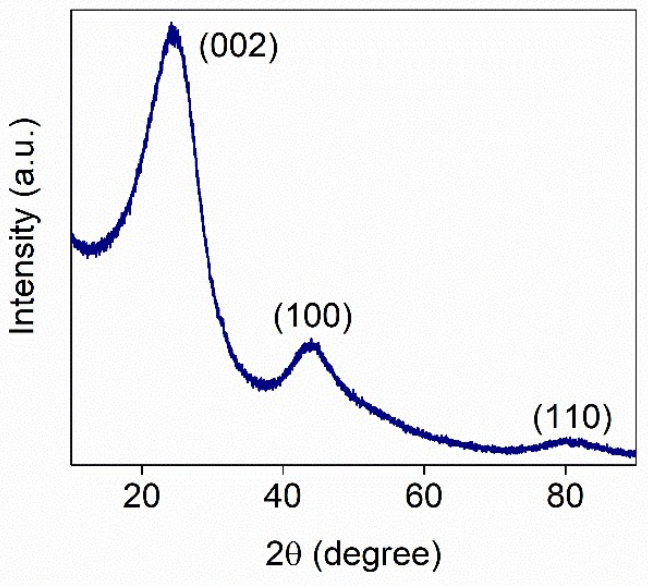

Figure S6. XRD patterns of CFs.

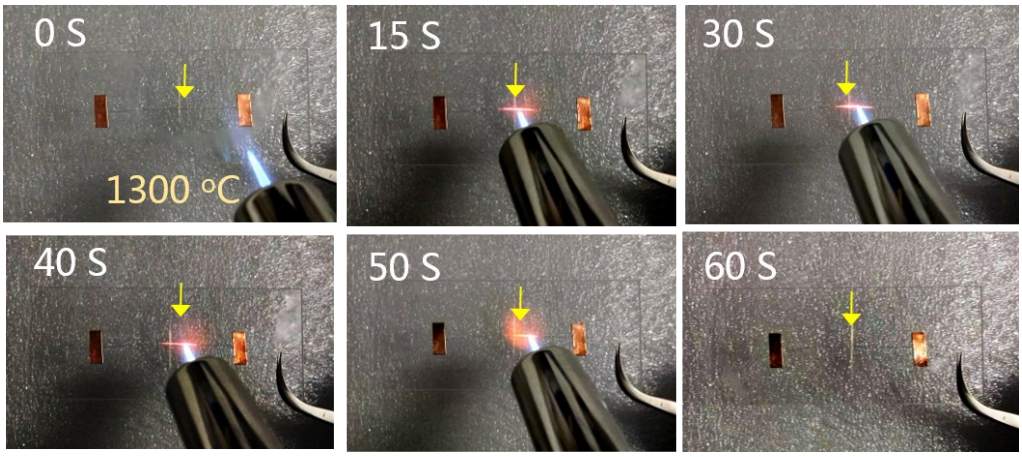

Figure S7. Illustration of the fire-retardant property of the CFs by firing a single CF with a butane gas burner (flame temperature ~ 1300 °C) for 60 seconds. Its original state can be well-preserved even after burning for 60 s.

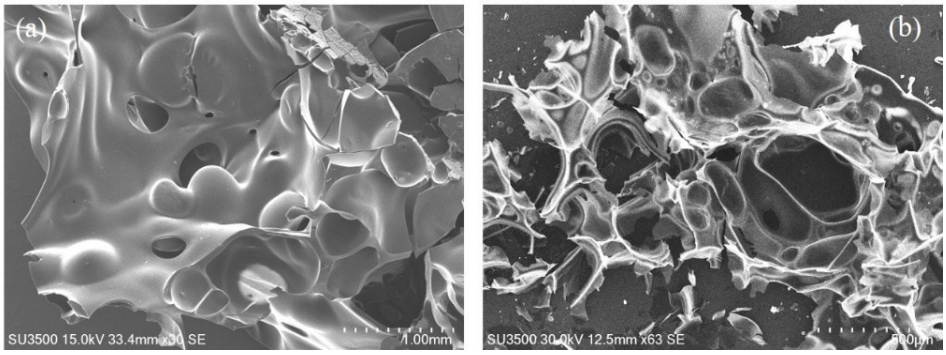

Figure S8. SEM images of the obtained carbon cracks.

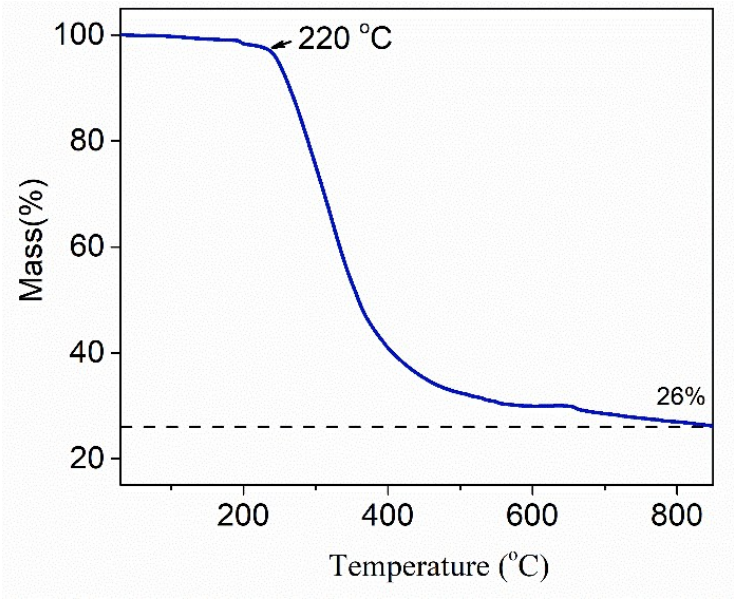

Figure S9. Thermogravimetric analysis (TGA) curve of "human hairs". The decomposition temperature was found to be ~220 °C.

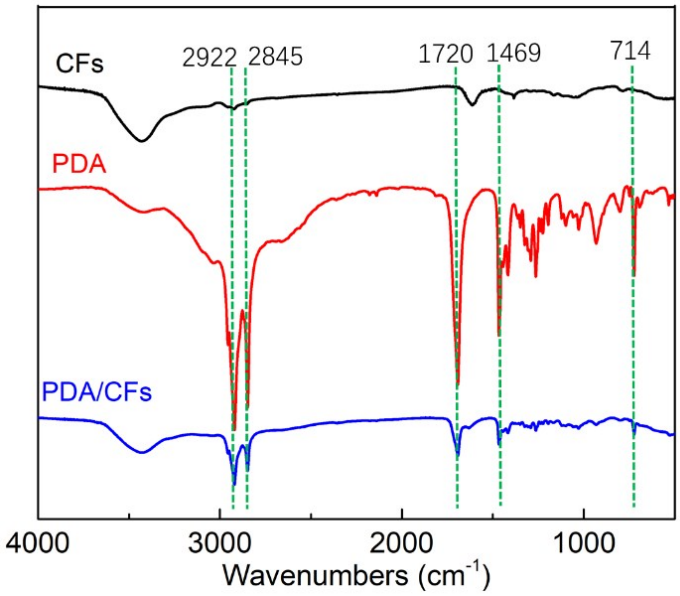

Figure S10. FTIR spectra of CFs, PDA and PDA/CFs.

As shown in Figure S10, after PDA coating, the characteristic peaks of PDA[S2-3], such as methylene non-symmetric stretch vibration at 2922 cm^{-1}, methylene symmetric stretch vibration at 2845 cm^{-1}, methylene non-symmetric angle vibration at 1469 cm^{-1}, the methylene swing in plane vibration at 714 cm^{-1} and the C=O stretching vibration at 1720 cm^{-1} were clearly observed in PDA/CFs, which clearly demonstrated the successfully coating PDA on CFs.

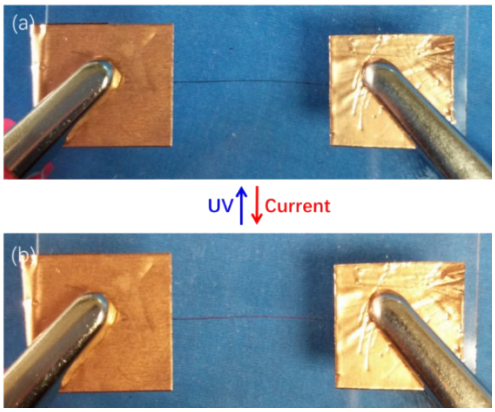

Figure S11. Digital photographs of (a) blue PDA/CF and (b) red PDA/CF, respectively, which demonstrated the reversibly switchable color transition under alternating currents from 5 mA to 30 mA at 45 Hz frequency and UV light stimuli. The minimum observable chromatic transition current (from blue to red) is found to be 7 mA with a response time of 10 s for a 2 μm thickness of PDA layer on PDA/CF and a rapid color transition from red to blue under UV-light stimuli is ~15 s. Noted that the chromatic transition time of PDA/CF is dramatically enhanced to ~0.2 s while the alternating current is increased to 15 mA. Similar to direct current stimuli, the red color stimulated by alternating currents can also be well-maintained even after the removal of the currents supply.

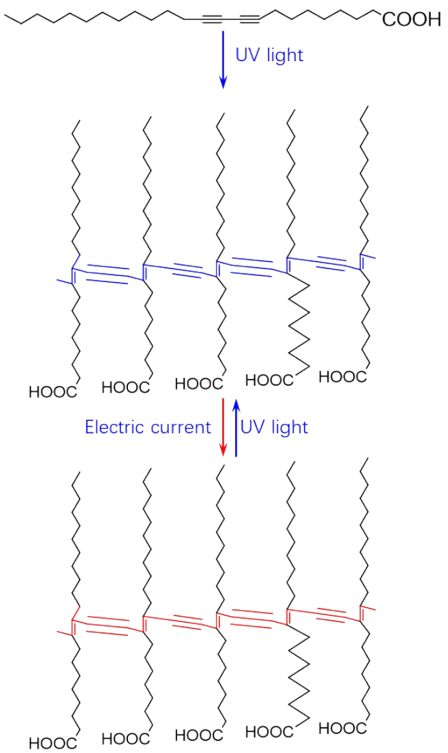

Figure S12. Schematic illustration of topochemical polymerization and color changes of resultant PDA.

Table S1. Morphologies of the reported carbon materials derived from "human hairs"

Carbonization condition (°C / hour)	Morphology	Reference
700,800 and 900 °C / 2 h	Carbon flakes	S4
550, 650 and 750 °C / 1 h	Carbon powder	S5
600, 800,1000 and 1100 °C / 3 h	Carbon powder	S6
900 °C / 3 h	Carbon cracks and powder	S7
600, 700, 800 and 900 °C / 2 h	Carbon powder	S8
700 °C / 2 h	Carbon powder	S9
850 °C / 6 h	Carbon powder	S10
650, 550 and 750 °C / 1 h	Carbon cracks and powder	S11
750 °C / 3 h	Carbon powder	S12
900 °C / 2 h	Carbon powder	S13
Below 350 °C / 2 h	Carbon microtube	S14
Above 350 °C	Carbon cracks	S14
800 °C / 2 h	Carbon powder	S15

Table S2. Response time and reversibility of the PDA/CFs under current and UV stimuli

Current (mA)	7	10	15	30	35
Response Time (s)	8	3	0.2	/	/
UV Time (s)	13	13	15	19	/
Temperature (^{o}C)	12	13.6	15.4	45.6	58
Reversibility	Reversible	Reversible	Reversible	Reversible	Irreversible

Note that: The response time is difficult to be accurately determined while the passing current is over 15 mA due to the ultrafast color transition; In addition, the color transition becomes irreversible when the passing current is over 35 mA.

References:

(1) Robbins, C.R. Chemical and Physical Behavior of Human Hair, Springer-Verlag Berlin Heidelberg, 1994.

(2) K. Wang, M. Liua, C. Song, L. Shen, P. Chena, S. Xu, *Materials and Design*, Surface-conductive UHMWPE fibres via in situ reduction and deposition of graphene oxide2018, **148**, 167–176.

(3) R. Luo, L. Tang, J. Wang, Y. Zhao, Q. Tu, Y. Weng, R. Shen, N. Huang, Improved immobilization of biomolecules to quinone-rich polydopamine for efficient surface functionalization, *Colloids and Surfaces B: Biointerfaces,* 2013*,* **106**, 66–73.

(4) Qian, W.; Sun, F.; Xu, Y.; Qiu, L.; Liu, C.; Wang, S.; Yan, F. Human Hair-Derived Carbon Flakes for Electrochemical Supercapacitors. *Energy Environ. Sci.* **2014**, *7*, 379-386.

(5) Zhao, Z.; Xiao, P.; Zhao, L.; Liu, Y.; Han, B. Human Hair-Derived Nitrogen and Sulfur Co-Doped Porous Carbon Materials for Gas Adsorption. *RSC Adv.* **2015**, *5*, 73980-73988.

(6) Chaudhari, K. N.; Song, M. Y.; Yu, J. Transforming Hair into Heteroatom-Doped Carbon with High Surface Area. *Small* **2014**, *10*, 2625–2636.

(7) Yu, M.; Li, R.; Tong, Y.; Li, Y.; Li, C.; Hong, J.; Shi, G. A Graphene Wrapped Hair-Derived Carbon/Sulfur Composite for Lithium–Sulfur Batteries. *J. Mater. Chem. A* **2015**, *3*, 9609-9615.

(8) Liu, X.; Zhou, W.; Yang, L.; Li, L.; Zhang, Z.; Ke, Y.; Chen, S. Nitrogen and Sulfur Co-Doped Porous Carbon Derived From Human Hair as Highly Efficient Metal-Free Electrocatalysts for Hydrogen Evolution Reactions. *J. Mater. Chem. A* **2015**, *3*, 8840-8846.

(9) Ou, J.; Zhang, Y.; Chen, L.; Yuan, H.; Xiao, D. Heteroatom Doped Porous Carbon Derived From Hair as an Anode with High Performance for Lithium Ion Batteries. *RSC Adv.* **2014**, *4*, 63784-63791.

(10) Sahasrabudhe, A.; Kapri, S.; Bhattacharyya, S. Graphitic Porous Carbon Derived From Human Hair as 'Green' Counter Electrode in Quantum Dot Sensitized Solar Cells. *Carbon* **2016**, *107*, 395-404.

(11) Zhao, Z.; Xiao, P.; Zhao, Li.; Liu, Y.; Han, B. Human Hair-Derived Nitrogen and Sulfur Co-Doped Porous Carbon Materials for Gas Adsorption. *RSC Adv.* **2015**, *5*, 73980-73988.

(12) Satish, R.; Aravindan, V.; Ling, W. C.; Woei, N. K.; Madhavi, S. Macroporous Carbon From Human Hair: A Journey Towards the Fabrication of High Energy Li-ion Capacitors.

Electrochimica Acta 2015, *182*, 474–481.

(13) Sun, G.; Zhou, L.; Li, J.; Tang, J.; Wang, Y. Human Hair-Derived Graphene-Like Carbon Nanosheets to Support Pt Nanoparticles for Direct Methanol Fuel Cell Application. *RSC Adv.* 2015, *5*, 71980-71987.

(14) Im, D. S.; Kim, M. H.; Jung, H.; Park, W. H. Formation and Characterization of Hollow Microtubes by Thermal Treatment of Human Hair. *ACS Sustainable Chem. Eng.* 2018, *6*, 6350-6357.

(15) Saravanan, K. R.; Kalaiselvi, N. Nitrogen Containing Bio-Carbon as a Potential Anode for Lithium Batteries. *Carbon*, 2015, *81*, 43-53.