Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic Supplementary Information

In situ Growth-mediated Bacterial nanocellulose-based Flexible Supercapacitor

Qisheng Jiang[1], Clayton Kacica[2], Thiagarajan Soundappan[3], Kengku Liu[1], Sirimuvva Tadepalli[1], Pratim Biswas[2], Srikanth Singamaneni[1,*]

1 Department of Mechanical Engineering and Materials Science, Institute of Materials Science and Engineering, Washington University in St. Louis 1 Brookings Dr., St. Louis, MO 63130

2 Department of Energy, Environmental and Chemical Engineering, Washington University, St. Louis, MO 63130

3 School of Science, Navajo Technical University, Crownpoint, NM, 87313, USA

*E-mail: singamaneni@wustl.edu (SS), pbiswas@wustl.edu (PB)

Experimental methods

Materials: Graphite flakes, PEDOT:PSS solution (Orgacon™ HIL-1005, 1 wt% in water, high conductivity grade), hypophosphorous acid (HPA) and all chemicals for bacterial medium are purchased from Sigma-Aldrich. *Gluconacetobacter hansenii* was purchased from ATCC (ATCC® 53582).

Preparation of RGO/PEDOT:PSS/BNC electrodes: *Gluconacetobacter hansenii* (ATCC®53582) was cultured in test tubes containing 16 ml of #1765 medium at 30°C under shaking at 250 rpm. The #1765 medium is composed of 2% (w/v) glucose, 0.5% (w/v) yeast extract, 0.5% (w/v) peptone, 0.27% (w/v) disodium phosphate, and 0.5% (w/v) citric acid. Graphene oxide was synthesized using an improved method reported by Tour and coworkers. Graphene oxide solution (28 mL of 0.1wt%) was centrifuged and redispersed in #1765 medium and then centrifuged again to leave a wet mixture of GO and medium after decanting supernatant. Bacterial culture solution (incubated 3 days) and 2 ml of 1 wt% PEDOT:PSS (Sigma Aldrich) was added to the GO/medium wet mixture to make it to a total 8ml (with GO concentration of 0.35 wt%, PEDOT:PSS concentration of 0.25 wt%). The solution was subsequently transferred to petridish (diameter: 6 cm) and incubated at room temperature without disturbance for 5 days to obtain a GO/PEDOT:PSS/BNC semi-dry film. For purification, the film was harvested from the petri dish and washed in a 500 ml of 0.1 M NaOH aqueous solution under boiling condition for 2 h. The GO/PEDOT:PSS/BNC hydrogel was then dialyzed in nanopure water for 2 days. The as cleaned hydrogel was then immersed in 5 wt% HPA and then heated to 60 °C for 24 hours, dialyzed in nanopure water and dried under ambient conditions. To show the scalability of the fabrication technique, a large electrode was prepared in a Pyrex bakeware (18×18 cm) in the same manner mentioned above.

Preparation of flexible all-solid state supercapacitors: A PVA/H_2SO_4 gel electrolyte was prepared by mixing 3 g of PVA powder, 3 g of H_2SO_4, and 30 mL nanopure water together, and then heated to 85 °C under vigorous stirring until the solution became clear. After the solution cooled down to room temperature, two pieces of RGO/PEDOT:PSS/BNC electrodes and a BNC paper as separator were immersed into the PVA/H_2SO_4 gel for 10 mins and they were assembled into a flexible all- solid state device. The device was dried overnight in fume hood to remove excess water.

Microstructure characterization and properties measurement: Scanning electron microscope (SEM) images were obtained using a FEI Nova 2300 Field Emission SEM at accelerating voltage of 10kV. Atomic force microscopy (AFM) images were obtained using Dimension 3000 (Bruker Inc.) in light tapping mode. Raman spectra were obtained using a Renisha inVia confocal Raman spectrometer mounted on a Leica microscope with 50x objective and 785 nm wavelength diode laser as an illumination source. XPS analysis was performed using Physical Electronics® 5000 VersaProbe II Scanning ESCA (XPS) Microprobe.

Electrochemical characterizations: Cyclic voltammetry (CV) and galvanostatic charge/discharge studies analysis were carried out using CHI 760 bipotentiostat (CH Instruments, Austin, USA). Chronopotentiometry technique used to run the charge/discharge measurements in the potential range from 0 to 0.8 V. Electrochemical studies were carried out using three electrode and two electrode configurations (solid-state device). In three electrode setup, RGO/PEDOT:PSS/BNC composite served as working electrode, Ag/AgCl as reference, and platinum wire as counter electrode. The electrolyte solution used here is 1 M H_2SO_4.

Preparation of PEDOT:PSS/BNC, GO/BNC and rGO/BNC films: PEDOT:PSS/BNC film was prepared by adding 2ml of 1 wt% PSS:PEDOT solution to 6ml BNC culture solution (overall 8ml, the concentration of PSS:PEDOT in solution is 0.25 wt%. After 5 days, the hydrogel was harvested and cleaned in the manner discussed above. GO/BNC film was prepared by adding a mixture of BNC culture solution and graphene oxide solution (overall 8ml), the concentration of GO in solution is 0.3 wt%. After 5 days, the hydrogel was harvested and cleaned in the manner discussed above. RGO/BNC film was prepared by adding a mixture of BNC culture solution and graphene oxide solution (overall 8ml, the concentration of GO in solution is 0.3 wt%. After 5 days, the hydrogel was harvested, cleaned, dried and reduced in the manner mentioned above.

Calculation details: The mass specific capacitances ($C_{s,\,CV}$) of the electrodes and device are all calculated from CV profile by the equation below:

$$C_{s,\,CV} = \frac{I_a - I_c}{m * (dV/dt)}$$

where I_a, I_c, m, and dv/dt are the anodic current, cathodic current, electrode mass, and scan rate, respectfully.

The mass specific capacitances ($C_{s,\,C\text{-}D}$) of the electrodes and device are all calculated from GCD profiles by the equation below:

$$C_{s,\,C-D} = \frac{I\Delta t}{m\Delta V}$$

Where *I, Δt, m, ΔV* are the applied current, the elapsed time, the mass of the electrode, and the voltage range, respectfully.

Supporting figures

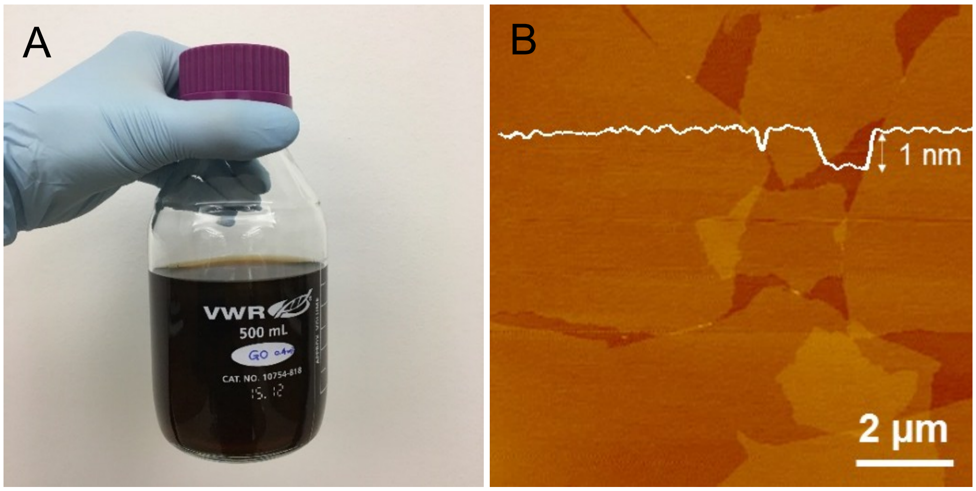

Figure S1. (A) Picture of a bottle of GO solution. (B) AFM image of GO flakes deposited on a silicon substrate.

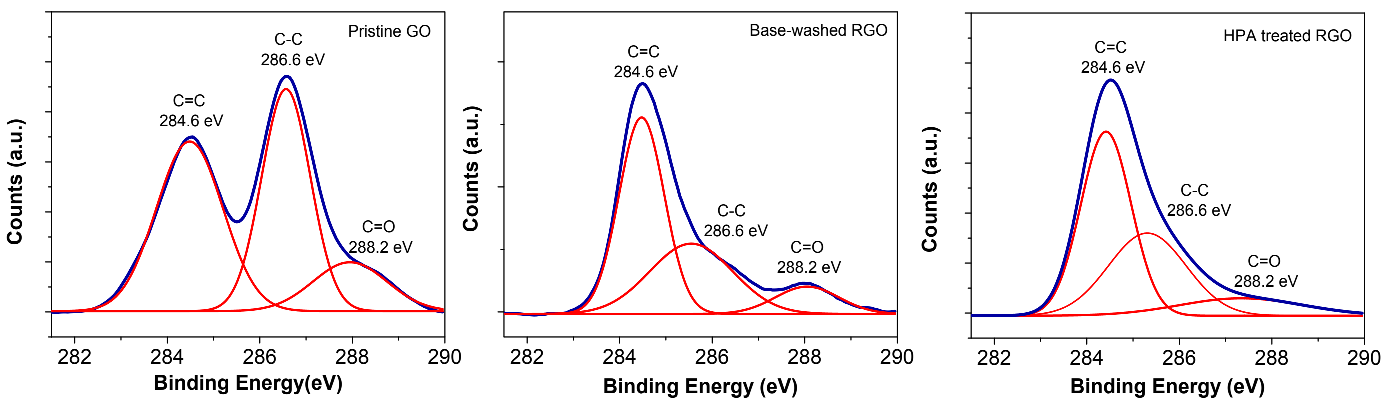

Figure S2. XPS spectra of pristine GO, base-washed RGO and HPA-treated RGO.

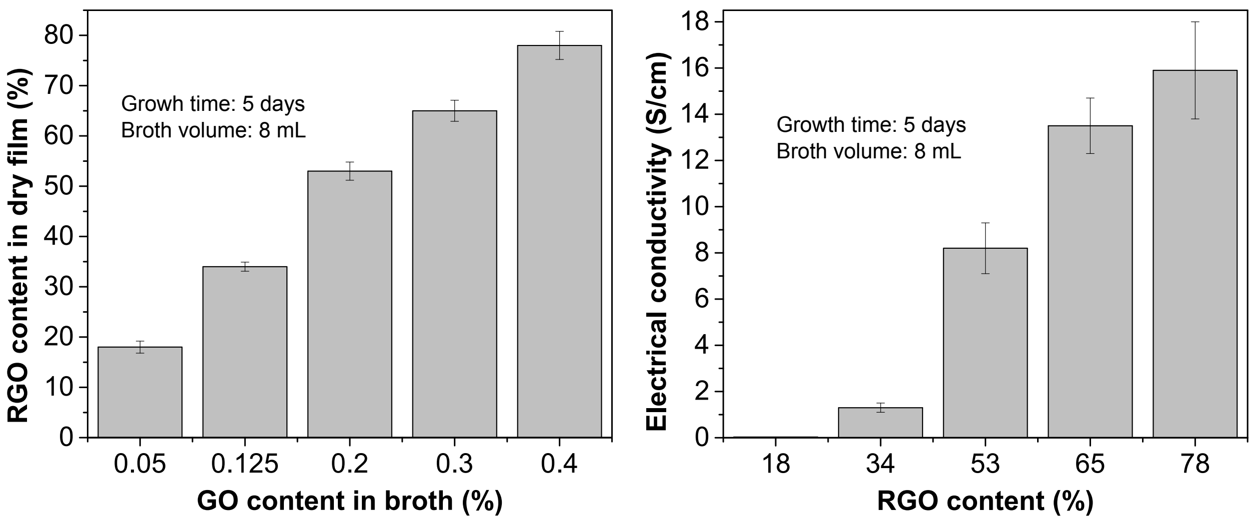

Figure S3. RGO content in dry film can be tuned by varying GO content in broth. Electrical conductivity of RGO/BNC films with various RGO contents.

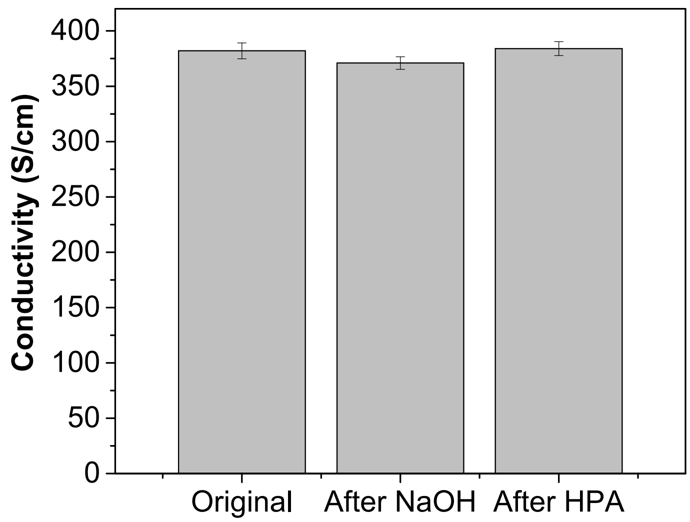

Figure S4. Effect of solution processes on pristine PEDOT:PSS deposited on a silicon substrate.

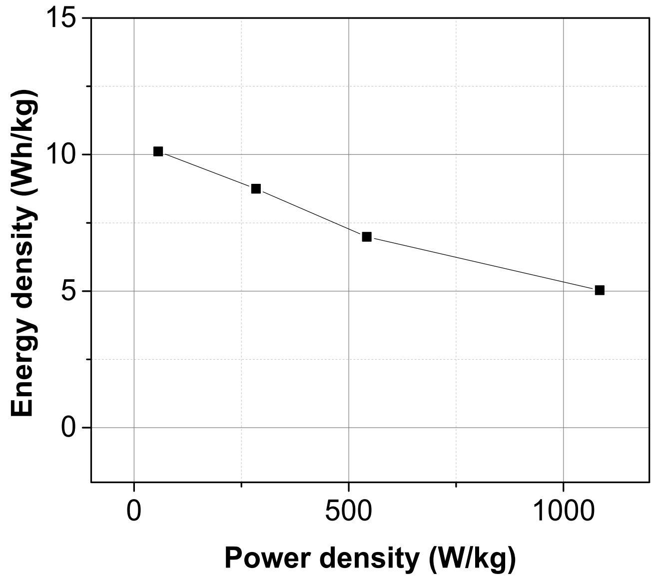

Figure S5. Specific energy and power densities of the Flexible device.

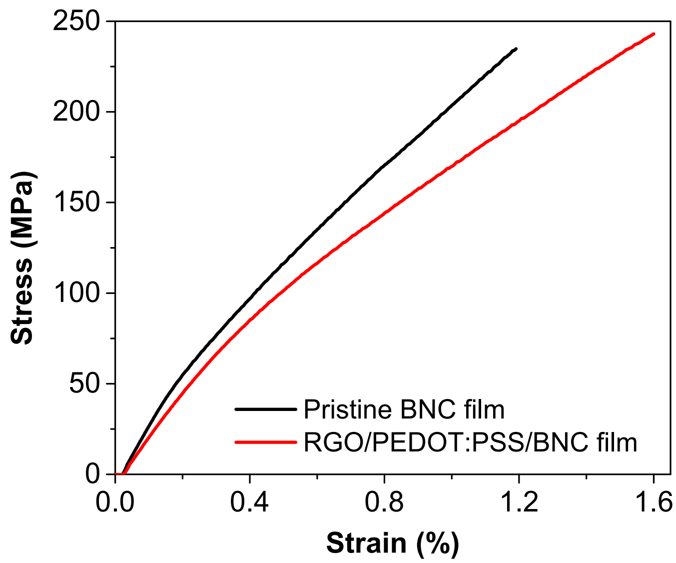

Figure S6. Strain-stress curve of pristine BNC and RGO/PEDOT:PSS/BNC.

Table S1: The comparison of recent flexible paper- based and some carbon-based supercapacitors. (NA: not available)

Material name	Electrolyte	Electrode Capacitance	Current collector for device
PEDOT on RGO[1]	NA	108 F g^{-1} at 0.3 A g^{-1}	NA
PEDOT:PSS-RGO film[2]	1 M H_3PO_4	52.7 F g^{-1} at 10 mV s^{-1}	Yes
PANI- BNC paper[3]	1 M H_2SO_4	273 F g^{-1} at 0.2 A g^{-1}	NA
PEDOT-paper[4]	1 M H_2SO_4	115 F g^{-1} at 0.4 A g^{-1}	No
CNT-BNC paper[5]	1 M H_2SO_4	50.5 F g^{-1} at 1 A g^{-1}	No
Graphene-cellulose paper[6]	1 M H_2SO_4	120 F g^{-1} at 1 mV s^{-1}	Yes
PANI-Au paper[7]	1 M H_2SO_4	212 F g^{-1} at 0.2 A g^{-1}	Yes
BNC-MWCNTs-PANI paper[8]	1 M H_2SO_4	656 F g^{-1} at 1 A g^{-1}	No
Graphite/Ni/Co_2NiO_4- paper[9]	1 M H_2SO_4	734 mF cm^{-2} at 5 mV s^{-1}	Yes
CNTs/MnO_2/CNTs paper[10]	1 M Na_2SO_4	327 F g^{-1} at 10 mV s^{-1}	No
PPy@nanocellulose paper[11]	2 M NaCl	185 F g^{-1} at 2 mA cm^{-2}	Yes
p-BC@MnO2 paper[12]	1 M Na_2SO_4	173.32 F g^{-1} at 1 A g^{-1}	Yes
This work	PVA-H_2SO_4	373 F g^{-1} at 1 A g^{-1}	No

References

1. Zhang, J.; Zhao, X. S., Conducting Polymers Directly Coated on Reduced Graphene Oxide Sheets as High-Performance Supercapacitor Electrodes. *The Journal of Physical Chemistry C* **2012,** *116* (9), 5420-5426.
2. Liu, Y.; Weng, B.; Razal, J. M.; Xu, Q.; Zhao, C.; Hou, Y.; Seyedin, S.; Jalili, R.; Wallace, G. G.; Chen, J., High-Performance Flexible All-Solid-State Supercapacitor from Large Free-Standing Graphene-PEDOT/PSS Films. *Scientific Reports* **2015,** *5*, 17045.
3. Wang, H.; Zhu, E.; Yang, J.; Zhou, P.; Sun, D.; Tang, W., Bacterial Cellulose Nanofiber-Supported Polyaniline Nanocomposites with Flake-Shaped Morphology as Supercapacitor Electrodes. *The Journal of Physical Chemistry C* **2012,** *116* (24), 13013-13019.
4. Anothumakkool, B.; Soni, R.; Bhange, S. N.; Kurungot, S., Novel scalable synthesis of highly conducting and robust PEDOT paper for a high performance flexible solid supercapacitor. *Energy & Environmental Science* **2015,** *8* (4), 1339-1347.
5. Kang, Y. J.; Chun, S.-J.; Lee, S.-S.; Kim, B.-Y.; Kim, J. H.; Chung, H.; Lee, S.-Y.; Kim, W., All-Solid-State Flexible Supercapacitors Fabricated with Bacterial Nanocellulose Papers, Carbon Nanotubes, and Triblock-Copolymer Ion Gels. *ACS Nano* **2012,** *6* (7), 6400-6406.
6. Weng, Z.; Su, Y.; Wang, D.-W.; Li, F.; Du, J.; Cheng, H.-M., Graphene–Cellulose Paper Flexible Supercapacitors. *Advanced Energy Materials* **2011,** *1* (5), 917-922.
7. Yuan, L.; Xiao, X.; Ding, T.; Zhong, J.; Zhang, X.; Shen, Y.; Hu, B.; Huang, Y.; Zhou, J.; Wang, Z. L., Paper-Based Supercapacitors for Self-Powered Nanosystems. *Angewandte Chemie International Edition* **2012,** *51* (20), 4934-4938.
8. Li, S.; Huang, D.; Zhang, B.; Xu, X.; Wang, M.; Yang, G.; Shen, Y., Flexible Supercapacitors Based on Bacterial Cellulose Paper Electrodes. *Advanced Energy Materials* **2014,** *4* (10), 1301655-n/a.
9. Feng, J.-X.; Ye, S.-H.; Wang, A.-L.; Lu, X.-F.; Tong, Y.-X.; Li, G.-R., Flexible Cellulose Paper-based Asymmetrical Thin Film Supercapacitors with High-Performance for Electrochemical Energy Storage. *Advanced Functional Materials* **2014,** *24* (45), 7093-7101.
10. Gui, Z.; Zhu, H.; Gillette, E.; Han, X.; Rubloff, G. W.; Hu, L.; Lee, S. B., Natural Cellulose Fiber as Substrate for Supercapacitor. *ACS Nano* **2013,** *7* (7), 6037-6046.
11. Wang, Z.; Tammela, P.; Zhang, P.; Huo, J.; Ericson, F.; Stromme, M.; Nyholm, L., Freestanding nanocellulose-composite fibre reinforced 3D polypyrrole electrodes for energy storage applications. *Nanoscale* **2014,** *6* (21), 13068-13075.
12. Chen, L.-F.; Huang, Z.-H.; Liang, H.-W.; Guan, Q.-F.; Yu, S.-H., Bacterial-Cellulose-Derived Carbon Nanofiber@MnO2 and Nitrogen-Doped Carbon Nanofiber Electrode Materials: An Asymmetric Supercapacitor with High Energy and Power Density. *Advanced Materials* **2013,** *25* (34), 4746-4752.