

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Electronic Supporting Information (ESI)

Bio-inspired Beehive-like Hierarchical Nanoporous Carbon Derived from Bamboo-based Industrial Byproduct as High Performance Supercapacitor Electrode Material

Weiqian Tian,^a Qiuming Gao,^{a*} Yanli Tan,^a Kai Yang,^a Lihua Zhu,^a Chunxiao Yang,^a and Hang Zhang^a

^a Key Laboratory of Bio-inspired Smart Interfacial Science and Technology of Ministry of Education, Beijing Key Laboratory of Bio-inspired Energy Materials and Devices, School of Chemistry and Environment, Beihang University, Beijing100191, People's Republic of China.

Email: qmgao@buaa.edu.cn.

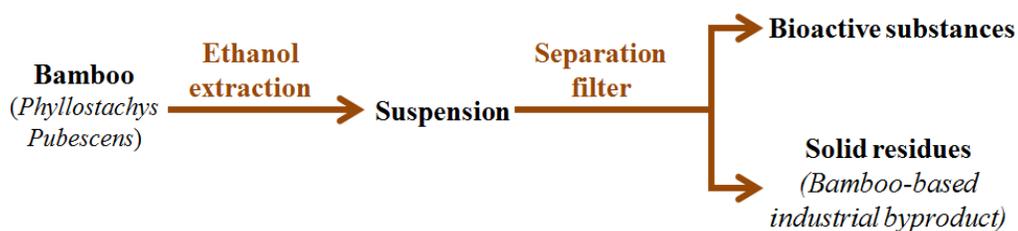


Figure S1. Flow diagram of extract bioactive substances from the bamboo (*Phyllostachys pubescens*) in Yunnan of China.

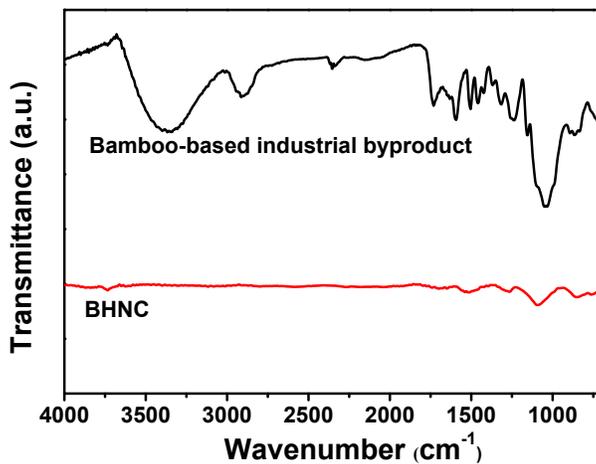


Figure S2. IR spectra of bio-inspired beehive-like hierarchical nanoporous carbon (BHNC) and the bamboo-based industrial byproduct.

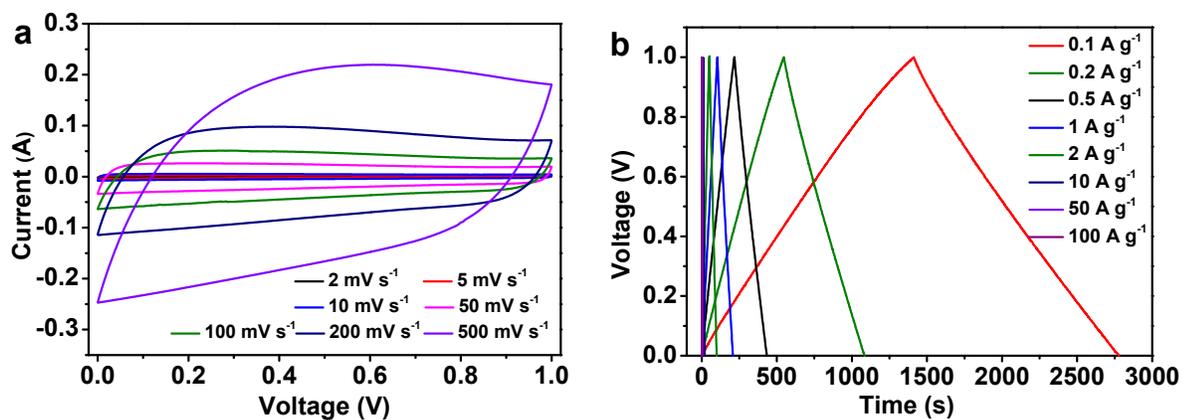


Figure S3. (a) Cyclic voltammetry and (b) galvanostatic charge/discharge of BHNC-based symmetrical supercapacitors in 6 M KOH.

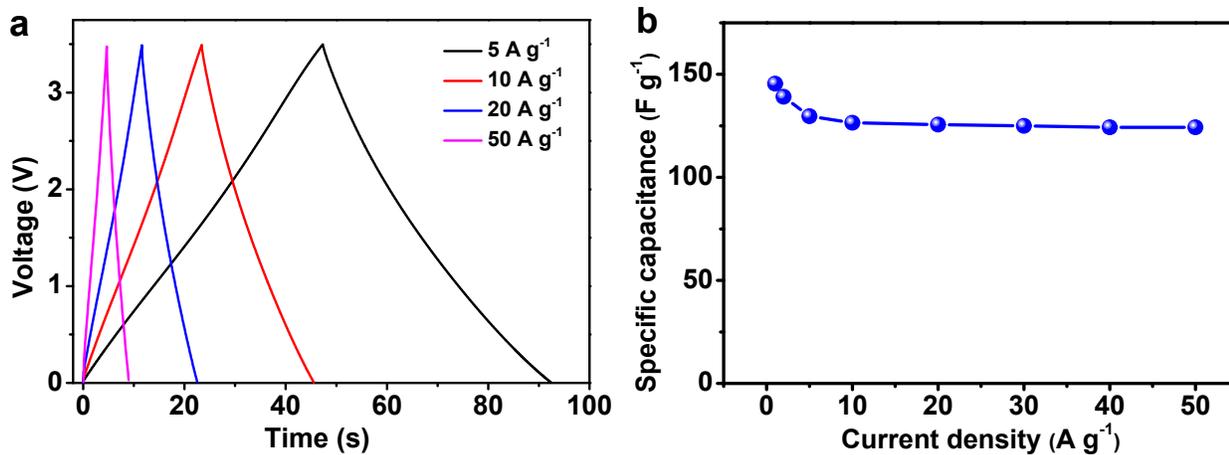


Figure S4. (a) Galvanostatic charge/discharge curves at different current densities and (b) the charge/dicharge rate performance of the control sample with vacuum annealing at 1000°C in the EMIM TFSI electrolytes. 85.5% capacitance value of the control sample was retained at 50 A g⁻¹.

In addition, for further demonstrate that the good match between the size of electrolyte ions and pore sizes can enhance the electrode performances, a BHNC-based symmetric supercapacitor using another ionic liquid of BMPY TFSI (BMPY⁺ of 1.1 nm and TFSI⁻ of 0.29 nm) as electrolyte was discussed. Figure S5 shows that the cells in BMPY TFSI system exhibit the distorted CV curves and low specific capacitance compared with that in the EMIM TFSI system at the same conditions, due to the larger cationic ion diameter than most of the pore size of BHNC which leads to inefficient electrolyte ion transport and a high equivalent series resistance.

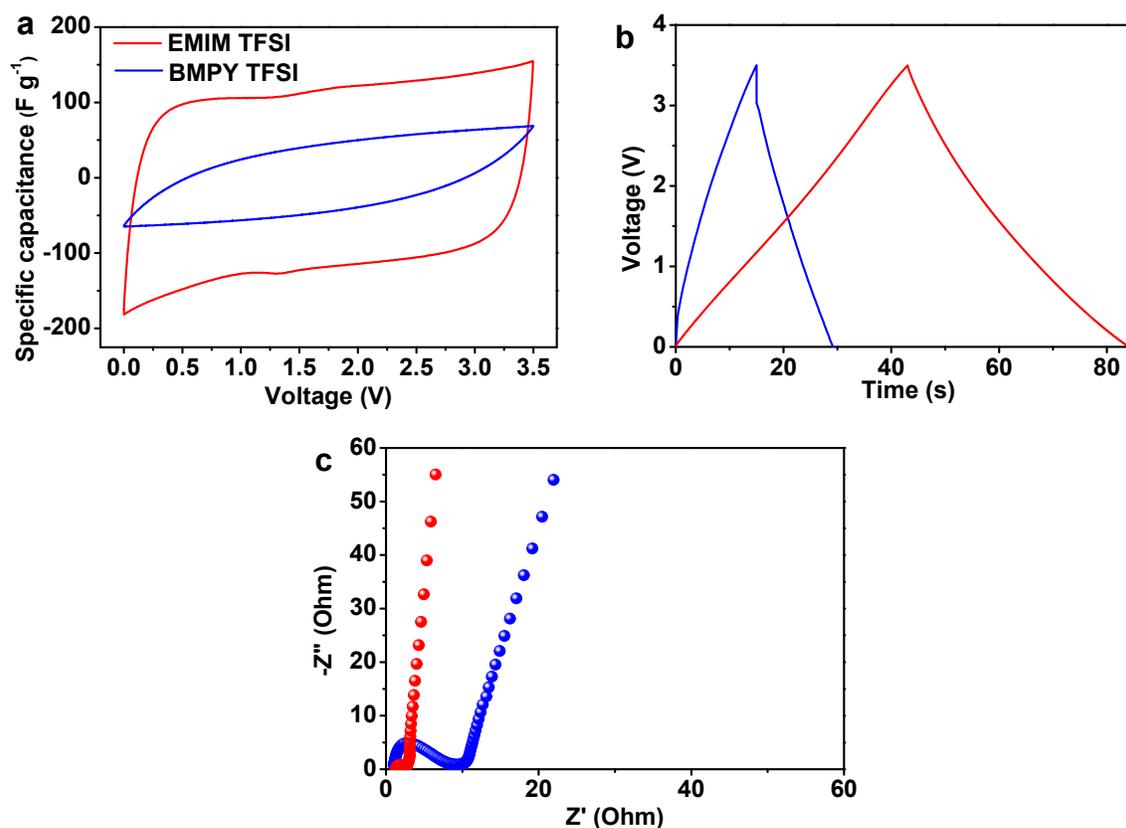


Figure S5. (a) CV curves at $5\ mV\ s^{-1}$, (b) galvanostatic charge-discharge curves at $5\ A\ g^{-1}$ and (c) the Nyquist plot of the BHNC-based electrode in two-electrode system with different ionic liquid electrolytes.

We also further confirm the key role of the beehive-like hierarchical microporous structures on the interconnected carbon nanosheet frameworks to enhance the electrochemical application. A control sample was synthesised by direct pyrolysis of bamboo-based industrial byproducts at 800°C for 2 h without hydrothermal treatment, and other synthetic processes are the same as that of the BHNC. The porous texture was measured by nitrogen adsorption/desorption experiments. The N₂ adsorption-desorption isotherm and the pore size distribution deduced by the NLDFT method are shown in Figure S6a and b. It is clear that the control sample only owns a narrow micropore system with the pore size around 0.54 nm (96% micropore volume) without the wide range meso/macro-pore system, and its specific surface area value (1106 m² g⁻¹) is a little lower than that of the BHNC (1472 m² g⁻¹).

From the electrochemical characterization of the control sample in Figure S6d-f, it can be clearly seen that the control sample displays significant distorted CV curves at high scan rates and a lower capacitance response compared with that of the BHNC both in aqueous and ionic liquid systems under the same conditions, which are attributed to the fact that the control sample only possesses a narrow micropore system without the macro/meso-pore system to buffer vast electrolyte ions and thus owns an inefficiently ion transfer process at high scan rates.

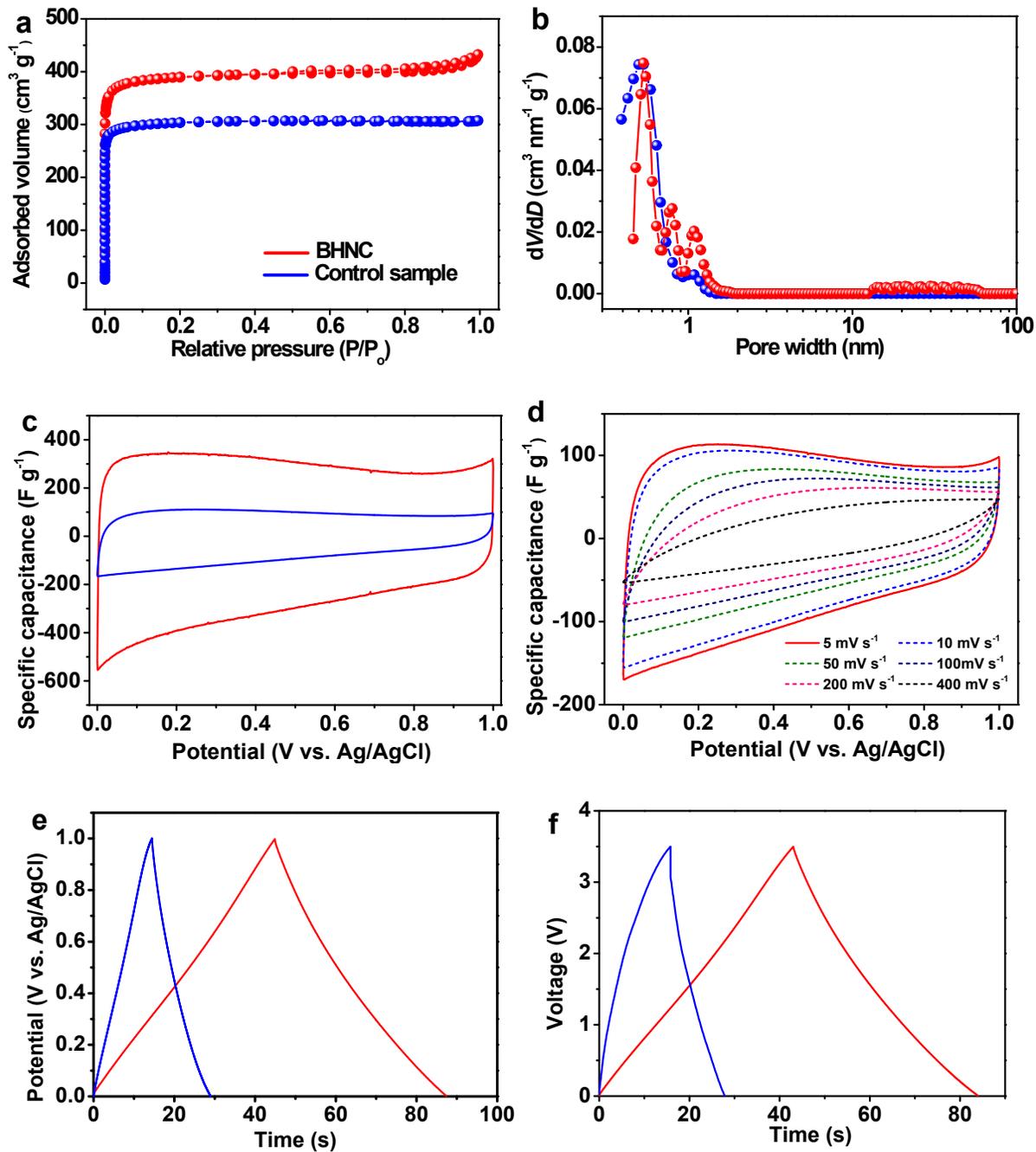


Figure S6. (a) Nitrogen sorption isotherms of BHNC and the control sample with the pore size distributions (b) deduced by the NLDFT method. (c) CV curves of BHNC and the control sample at a scan rate of 5 mV s^{-1} . (d) CV curves of the control sample at different scan rates. (e) Galvanostatic charge-discharge curves of BHNC and the control sample at 5 A g^{-1} in three-electrode configuration with 6 M KOH solution as electrolyte. And (f) galvanostatic charge-discharge curves of the samples at 5 A g^{-1} in two-electrode system with a ionic liquid of EMIM TFSI as electrolyte.

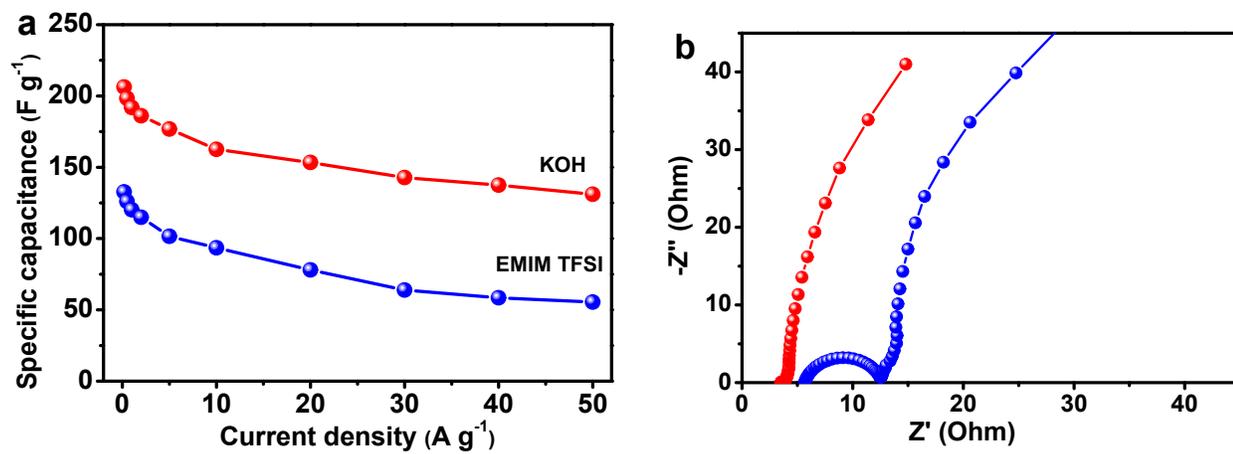


Figure S7. (a) The charge/dicharge rate performance, and (b) the Nyquist plots of the control sample without vacuum annealing in either electrolyte.

We have also examined the effect of activation parameters (mass ratio of KOH/carbon, activation temperature and time) to optimize the synthetic process for enhancing the electrochemical performances. The relevant results are displayed in Figure S8. As to the activation process, the redox reaction ($6\text{KOH} + 2\text{C} \rightarrow 2\text{K} + 3\text{H}_2 + 2\text{K}_2\text{CO}_3$) between carbon source and KOH occurred at the temperature below 700°C generating the porous structure, and the K_2CO_3 can be completely decomposed ($\text{K}_2\text{CO}_3 \rightarrow \text{K}_2\text{O} + \text{CO}_2$) at around 800°C . The resulted CO_2 and K_2O can be further reduced by carbon to generate CO ($\text{CO}_2 + \text{C} \rightarrow 2\text{CO}$, $\text{C} + \text{K}_2\text{O} \rightarrow 2\text{K} + \text{CO}$) to further facilitate the generation of interconnected micropore networks through gas evaporation (CO_2 , CO). The metallic K can be intercalated between the carbon layers leading to the swelling of the carbon with a high pore volume.^{10, 59, 60} The increase of activation temperature can effectively improve both the specific surface area and pore volume leading to an enhanced capacitance. Moreover the increase of the mass ratio of KOH/carbon and activation time can also augment the porous microstructures and specific capacitance. However, higher activation temperature, mass ratio and activation time may cause the excess activation which result in the more broaden pore size distributions and larger pore diameters, which leading to decrease of the density and effective pore structures with decreasing of capacitance values.^{58, 59} It should be noted that the activation parameters of BHNC (mass ration of 1:1 at 800°C for 1 h) was optimized which is attributed to the comprehensive effect of complex activation reaction and district carbon precursor of bamboo fibers.

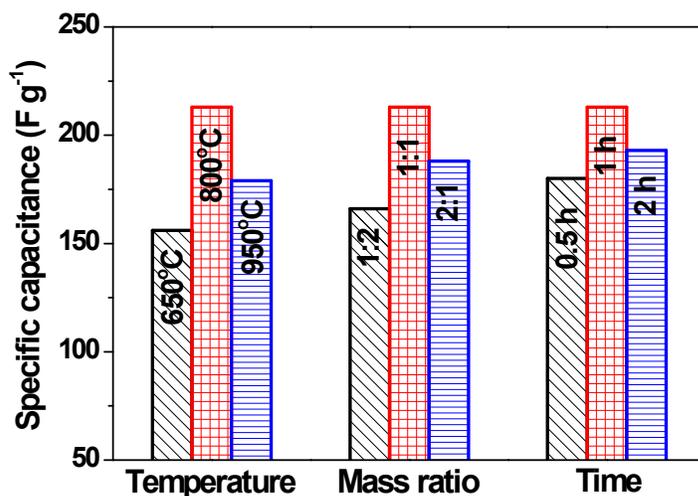


Figure S8. The specific capacitances of the samples prepared with different mass ratios of KOH/carbon (1:2, 1:1 and 2:1) at 800°C for 1 h, at different activation temperatures (650 , 800 and 950°C) with mass ratios of KOH/carbon (1:1) for 1 h, and for different activation 1 times (0.5 , 1 and 2 h) with mass ratios of KOH/carbon (1:1) at 800°C , respectively, at current density of 5 A g^{-1} .