Nanoelectronics and Its New Materials – A NEW ERA OF NANOSCIENCE

Nanoelectronics and Its New Materials -



Discover the recent advances in electronics research and fundamental nanoscience.

Nanotechnology has become the driving force behind breakthroughs in engineering, materials science, physics, chemistry, and biological sciences. In this compendium, we delve into a wide range of novel applications that highlight recent advances in electronics research and fundamental nanoscience. From surface analysis and defect detection to tailored optical functionality and transparent nanowire electrodes, this eBook covers key topics that will revolutionize the future of electronics.

To get your hands on this valuable resource and unleash the power of nanotechnology, simply download the eBook now. Stay ahead of the curve and embrace the future of electronics with nanoscience as your guide.



Seeing beyond





Capillary Evaporation on High-Dense Conductive Ramie Carbon for Assisting Highly Volumetric-Performance Supercapacitors

Qing Wang, Zhenyu Chen, Qitian Luo, Haijian Li, Jie Li, and Weiqing Yang*

Conductive biomass carbon possesses unique properties of excellent conductivity and outstanding thermal stability, which can be widely used as conductive additive. However, building the high-dense conductive biomass carbon with highly graphitized microcrystals at a lower carbonization temperature is still a major challenge because of structural disorder and low crystallinity of source material. Herein, a simple capillary evaporation method to efficiently build the high-dense conductive ramie carbon (hd-CRC) with the higher tap density of 0.47 cm³ g⁻¹ than commercialized Super-C45 (0.16 cm³ g^{-1}) is reported. Such highly graphitized microcrystals of hd-CRC can achieve the high electrical conductivity of 94.55 S cm⁻¹ at the yield strength of 92.04 MPa, which is higher than commercialized Super-C45 (83.92 S cm⁻¹ at 92.04 MPa). As a demonstration, hd-CRC based symmetrical supercapacitors possess a highly volumetric energy density of 9.01 Wh L^{-1} at 25.87 kW L^{-1} , much more than those of commercialized Super-C45 (5.06 Wh L^{-1} and 19.30 kW L⁻¹). Remarkably, the flexible package supercapacitor remarkably presents a low leakage current of 10.27 mA and low equivalent series resistance of 3.93 m Ω . Evidently, this work is a meaningful step toward high-dense conductive biomass carbon from traditional biomass graphite carbon, greatly promoting the highly-volumetric-performance supercapacitors.

1. Introduction

Biomass carbon obtained by anaerobic treatment have become the extremely potential electrode materials for energy storage

Q. Wang, Z. Chen, Q. Luo, W. Yang Key Laboratory of Advanced Technologies of Materials (Ministry of Education) School of Materials Science and Engineering Southwest Jiaotong University Chengdu 610031, China E-mail: wqyang@swjtu.edu.cn H. Li, J. Li, W. Yang Jinshi Technology Co. Ltd. 289 Longquanyi District, Chengdu 610100, China W. Yang Research Institute of Frontier Science Southwest Jiaotong University Chengdu 610031, China

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/smll.202303349

DOI: 10.1002/smll.202303349

devices because of their easily controlled property, naturally structural diversity, environmental friendliness, and rich sources.^[1–5] Generally, biomass precursors, composed of cellulose, hemicellulose, and lignin, play a vital role in the polymorphism of biomass carbon, affecting the graphitization degree of carbon materials.[6-9] Among them, cellulose derived carbon with parallel hydrogen bond network possesses the remarkable crystallinity for the improvement of electrical conductivity and the reduction of contact resistance between interfaces, and provides an efficiently convenient path for realizing the transmission role of internal electrolyte ions.^[10,11] Unfortunately, the existence of hemicellulose tremendously hinders the lateral growth of carbon crystals, and the presence of lignin extensively forms stable amorphous carbon.^[12,13] Therefore, it is still crucial for conductive biomass carbon to rationally develop the highly graphitized microcrystals (hGMCs).

Super-C45 as a commercial conductive carbon possesses the high conductivity, high thermal conductivity, high oxidation

stability, low density, etc., and have been widely applied into the field of conductive plastics, conductive rubber, conductive ink, and conductive additives.^[14-16] Especially for supercapacitors, Super-C45 plays a conductive role in achieving the outstanding rate performance.^[17-19] Unfortunately, its low tap density and easy agglomeration will intrinsically prolong the transmission path of electrolyte ions and occupy a certain volume of active electrode, badly limiting the application of highly-volumetricperformance supercapacitors.^[20] Recently, conductive biomass carbon with the resistivity of lower than 1 Ω cm possessed the advantages of higher tap density (>0.4 cm³ g⁻¹) than commercialized Super-C45 (0.16 cm³ g⁻¹).^[21,22] Their conductivities could be mainly ascribed to surface chemical composition, aggregate structure, porosity, and microcrystalline morphology.^[23] Among them, the rearrangement and growth of graphite-like microcrystals would tremendously restrict the rapid movement of π electrons.^[24] The improvement of graphitic degree will be conducive to the formation of excellently conductive network for further increasing its conductivity.^[25-27] To large-scaly fabricate the highly dense and highly graphitized conductive





Figure 1. Schematically structural diagram of high-dense conductive ramie carbon (hd-CRC). a) Optical photo of natural ramie with abundant cellulose. b) Strategy of preparing hd-CRC by pyrolysis after chemical stripping. c) Capillary evaporation on dense cellulose molecules. d) Representative SEM image of hd-CRC showing the obviously ordered structure. e) TEM image of hd-CRC revealing the hGMCs. f) Comparison diagram of physical properties on hd-CRC with commercialized Super-C45.

carbon is still an urgent problem to date. In this regard, hightemperature pyrolysis and precursor pretreatment methods were commonly employed to improve the graphitization degree of conductive biomass carbon.^[28] For the former, the increasement of carbonization temperature was conducive to expand the layer spacing of graphite-like structure and improved the order degree of disorderly turbine-layered nanodomain, but the hightemperature graphitization treatment badly reduced the yield and density of conductive biomass carbon. While for the latter, steam explosion, as the most commonly used method for precursor pre-treatment, could realize the separation and structural change of raw materials through chemical decomposition, mechanical splitting, and structural rearrangement of steam explosion materials, but it would cause the physical explosion of cellulose crystals.^[29] So far, there still lacks a gentle and controllable strategy to effectively extract the cellulose with complete crystal structure and to large-scaly prepare the high-dense conductive biomass carbon with hGMCs at a lower carbonization temperature.

Here, we report a simple capillary evaporation strategy to efficiently construct the high-dense conductive ramie carbon (hd-CRC) with a compacted density of 1.09 cm³ g⁻¹ and an electrical conductivity of 94.55 S cm⁻¹ at the yield strength of 92.04 MPa. This chemically stripped ramie precursor with ultra-high cellulose content (95.37%) effectively protect the crystal structure of cellulose, realizing the densification of cellulose molecules. Also, a large number of broken C–C bonds and C–H bonds from cellulose molecules will be re-organized and re-ordered to reconstruct substantial C=C bonds for the formation of hd-CRC with hGMCs. Furthermore, the hd-CRC–based symmetrical supercapacitors can deliver a high volumetric energy density of 15.82 Wh L⁻¹ at 780 W L⁻¹. Even at the high volumetric power density of 25.87 W L⁻¹, the device still has a volumetric energy

density of 9.01 Wh L⁻¹, much more than those of commercial Super-C45–based supercapacitor (5.06 Wh L⁻¹ and 19.30 kW L⁻¹). Attractively, 301.99 F flexible package supercapacitor possesses a low leakage current of 10.27 mA and low equivalent series resistance (ESR) of 3.93 m Ω , revealing hd-CRC as conductive additive can helpfully improve the electrochemical stability and volumetric performance of supercapacitor. This conductive biomass carbon based on chemically stripped ramie with ultrahigh cellulose content can not only wonderfully store the electrolyte ions, but also provide an effective transport path for ion diffusion during charging and discharging. Evidently, this hd-CRC can effectively improve the space volume ratio of active substances and obviously enhance the diffusion dynamics, synergistically promoting the cycle stability and rate performance of high volumetric supercapacitors.

2. Results and Discussion

Highly microcrystal-graphitized hd-CRC was synthesized by utilizing the capillary evaporation of cellulose molecules and then re-construction of C atoms during high-temperature pyrolysis. As shown in **Figure 1**a, the natural ramie with 72.43% cellulose, 19.8% hemicellulose, 0.7% lignin, and other water-soluble substance possesses the characteristics of highly mechanical strength, high crystallinity, high orientation, and excellent stability. In this work, Hydroxyl and superoxide anions produced by peroxyformic acid solution could depolymerize and dissolve lignin and hemicellulose in the ramie (Figure 1b).^[30] Generally, aromatic units could be most easily degraded into small fragments.^[31] Then, the exposed cellulose contained abundant hydroxyl groups to absorb a large amount of water molecules. In the subsequent capillary evaporation process, water molecules will gradually evaporate from the interior of cellulose molecules

to the surface, and the capillary force between nanocellulose bundles could cause them to aggregate and achieve densification.^[32] Attractively, the abundant hydroxyl groups on cellulose molecules could facilitate the formation of hydrogen bonds and increase intermolecular forces. Therefore, these chemically-stripped ramies with ultra-high cellulose content (95.37%) could effectively change the hydrogen-bond network formed by the interaction between hydroxyl groups through capillary evaporation (Figure 1c). Finally, the composition forms of C elements from the chemically-stripped ramies can orderly re-organize the C atoms and re-construct a large number of C=C bonds for the upsurge of graphite-like microcrystals. As shown in Figure S1, Supporting Information, obviously fibrous structure with an average diameter of 16 um on the surface of ramie can evidently prove the removal of lignin and hemicellulose by observing the destruction of cell wall. After carbonization atom recombination, the fibrous structure of hd-CRC can present the obviously ordered structure, and their average diameter of 6.5 µm can prove the reorganization of C atoms during pyrolysis (Figure 1d and Figure S2, Supporting Information). As shown in Figure 1e and Figure S3, Supporting Information, TEM images vividly revealed a hGMCs and randomly oriented pseudo-graphite structure, which could provide a large lumber of storage places for electrolyte ions and then benefit the electron transmission and ion diffusion. Based on it, we compared the physical properties of hd-CRC with commercialized Super-C45, such as tap density, electrical conductivity, compacted density, specific surface area (SSA), and pore volume (Figure 1f). As a result, the hd-CRC demonstrates the following excellent advantages: i) conductive ramie carbon with a high tap density of 0.47 cm³ g⁻¹ can effectively improve the volume proportion of active substances; ii) electrical conductivity of hd-CRC can peak at 94.55 S cm⁻¹ under the yield strength of 92.04 MPa; iii) compacted density of hd-CRC can achieve 1.09 cm³ g⁻¹ at the yield strength of 92.04 MPa; iv) hd-CRC possesses a prominent SSA of 219.50 m² g⁻¹ by using the BET method; v) pore volume of hd-CRC is $0.11 \text{ cm}^3 \text{ g}^{-1}$ by using the *t*-plot method, which can be conducive to reducing the absorption of electrolyte.

Also, hd-CRC with high density could be controllably prepared on a large scale. As shown in Figure 2a, the water bath process of natural ramie effectively removed the water-soluble substances of source material. This as-obtained ramie was fully immersed in the peroxyformic acid solution, and the peroxyformic acid molecules rapidly diffused into the fiber bundles. Among them, hydroxyl and peroxy group reacted with the aromatic ring on lignin to directly form the ester (Figure 2b). The extremely low lignin content properties of natural ramie quickly promoted to complete the oxidation process and its natural yellow eventually turned white. Subsequently, chemically stripped ramie precursors were obtained through the treatment of NaOH, achieving the purpose of degrading lignin and hemicellulose (Figure 2c and Figure S4, Supporting Information). Finally, 144.1 g hd-CRC was developed at once, corresponding the yield of 18.9% (Figure 2d). After the rough grinding and fine grinding, hd-CRC with high quality could be used as the conductive agent for the application of supercapacitors (Figure S5, Supporting Information). As shown in Figure 2e,f, natural ramie with cellulose, hemicellulose, lignin, and other water-soluble substance shows the obvious stripes and rough network structure. While the as-prepared chemically stripped ramie precursors

possess the smooth surfaces and hierarchically ordered structures (Figure 2g,h). Evidently, this capillary evaporation strategy can be used to regulate the capillary tension of cellulose molecules, which is beneficial for the further densifying and ordering of cellulose structures. Besides, the high-dense conductive ramie carbon could be controllably realized through the synergistic effect of high crystallinity on cellulose molecules and high-temperature re-organization on carbon atoms (Figure 2i,j). As shown in Figure 2k and Figure S6, Supporting Information, EDS analysis was used to prove the removal of impurity elements, such as Na, S, and Cl. In order to further determine the element types of hd-CRC, X-ray photoelectron spectroscopy (XPS) were applied to characterize the chemical composition and chemical bonds (Figure 2l and Figure S7, Supporting Information). Resulted, the atom proportion of carbon is increasing from 89.10% to 94.12% and graphite microcrystals are significantly improved, indicating that graphitization degree should be helpful to reduce the atom proportion of oxygen (Table S1, Supporting Information). According to the peak fitting of carbon element, C 1s spectrum is divided into four peaks at 284.80, 285.66, 288.75, and 291.37 eV, corresponding to the C=C/C-C, C-O, C=O, and O-C=O, respectively (Figure 2m).^[33] Among them, content of C=C peak is obviously higher than that of natural conductive ramie carbon (NCRC), presenting the greatly-improved crystallinity. This high crystallinity helpfully improves the thickness of pseudo-graphite layer (Table S2, Supporting Information). Additionally, relatively high proportion of C=O group can promote the water dispersion of carbon materials.

In order to determine the appropriate pyrolysis temperature of hd-CRC, thermogravimetric analysis of chemically stripped ramie precursors was employed to observe the decomposition of intermediates (Figure 3a). When the temperature was near 200 °C, the sample had a slight mass loss due to the removal of free moisture. While for the range of 280 to 380 °C, the mass loss of ramie precursors occurred, revealing to the rapid degradation of cellulose. Further, DTG curve presented a sharp peak, illustrative of the acceleration of thermal weight loss rate (Figure 3b). As shown in Figure 3c, the particle size distribution curve demonstrated the uniformity of hd-CRC and its overall average particle size was about 303.5 nm, benefiting the improvement of compaction density for electrode materials. XRD spectrum of hd-CRC showed two diffraction peaks at 22.4° and 43.3°, corresponding to the peak (002) and peak (100).^[34] Interestingly, the (002) diffraction peak moves to a higher angle with the increase of the pseudographite layer thickness. While (100) diffraction peak gradually sharpens, indicating that hd-CRC has a higher graphitization degree and a more ordered crystal structure (Figure 3d). Raman spectroscopy was used to study the defective density of carbon materials. Highly dense hd-CRC obviously showed two representative peaks at 1346 and 1591 cm⁻¹, corresponding to disordered sp³ hybrid carbon and graphitic sp² hybrid carbon, respectively (Figure 3e). The higher integral intensity ratio of hd-CRC (D/G = 2.56) than NCRC (D/G = 2.17) presents the more defects, revealing that chemically stripped process would result in the increase of defect density and the decrease of microcrystal size. FTIR spectroscopy was employed to characterize the surface functional groups of carbon materials. hd-CRC mainly exists in the form of C=C bond with tensile vibration, and other forms of bond are relatively few, such as C-H, C-O, and C=O, illustrating



www.small-journal.com

NANO · MICRO



Figure 2. Formative process and morphologies of hd-CRC. a) Photograph of natural ramie treated with water bath, b) chemically stripped process, c) chemically stripped ramie precursors through capillary evaporation, and d) hd-CRC subjected to rough grinding and fine grinding. e) Typical SEM image of natural ramie showing the obvious stripes and rough network structure. f) SEM image of natural ramie at low magnification, g) chemically stripped ramie precursors showing the hierarchically ordered structures, h) chemically stripped ramie precursors showing the smooth surfaces at low magnification, i) hd-CRC based on capillary evaporation and pyrolysis, and j) hd-CRC at low magnification. k) Element mapping images of hd-CRC for C element. I) XPS survey of hd-CRC. m) Fitting curve of C 1s.

the higher graphitization degree of hd-CRC, which is consistent with the results of XRD and TEM (Figure 3f).

Building parameter such as pyrolysis temperature can accurately regulate the graphitization degree, pore size distribution, and pore volume of conductive ramie carbon. As shown in **Figure 4**a,e,i, besides hd-CRC with amorphous and microcrystalline network, conductive ramie carbon such as highamorphous conductive ramie carbon (ha-CRC) with amorphous network and high-crystalline conductive ramie carbon (hc-CRC) with microcrystalline network can be successfully prepared at different pyrolysis temperature (800, 1000, and 1200 °C, respectively) via regulating the rearrangement of carbon atoms. The conductivity of conductive carbon black with low SSA had been proved to be beneficial for its graphitization degree.^[23] At a low pyrolysis temperature of 800 °C, the carbon atoms cannot be orderly rearranged due to the insufficient recombination driv-

CIENCE NEWS



Figure 3. Physical property of hd-CRC and NCRC. a) TGA curve of chemically stripped ramie precursor and natural ramie. b) DTG curve of chemically stripped ramie precursor and natural ramie. c) Nanoparticle size distribution. d) XRD pattern. e) Raman spectrum. f) FTIR curve.

ing force, resulting in a large number of amorphous structures (Figure 4c). According to the pore size distribution analysis, the SSA of ha-CRC is up to 276.31 $m^2 g^{-1}$ by BET method, mainly accompanied by a large number of mesopores (Figure 4d). Although h-ACRC with high SSA is beneficial to the storage of electrolyte ions, the existence of amorphous region hinders the transmission of electrons (Figure 4b). While at a high pyrolysis temperature like 1200 °C, carbon atoms can be orderly arranged to form a large number of graphite microcrystals (Figure 4k). Highly ordered arrangement of carbon atoms will cause the low SSA of 145.56 m² g⁻¹, accompanied by abundant micropores (Figure 4l). Although hc-CRC can contribute to the rapid transmission of electrons, the low SSA limits the effective storage of electrolyte ions (Figure 4j). Therefore, the preferred rearrangement of carbon atoms will be helpful to realize the coexistence of amorphous region and graphite microcrystalline region at a suitable pyrolysis temperature like 1000 °C (Figure 4g). Such 3D conductive networks exhibit high SSA of 219.50 m² g⁻¹ and suitable pore size distribution, promoting the improvement of charge transfer efficiency (Figure 4f,h).^[35]

As shown in **Figure 5**a, the tap density of hd-CRC prepared by wet milling is 0.47 cm³ g⁻¹, which is much higher than that of commercialized Super-C45 (0.16 cm³ g⁻¹). These two conductive materials simultaneously show the typical adsorption characteristics of type IV isotherm (Figure 5b). With the relative pressure of $P/P_0 < 0.1$, N₂ rapidly fills a large number of micropores, resulting in the increase of adsorption capacity. As shown in Figure 5c, pore volume of Super-C45 is about 0.12 cm³ g⁻¹ by *t*-plot method, and the SSA is only 85.61 m² g⁻¹ by BET method. Attractively, after the chemical stripping and capillary evapora-

tion, the SSA and pore volume of hd-CRC can rapidly increase to 219.50 m² g⁻¹ and 0.11 cm³ g⁻¹, respectively. Under the condition of yield strength, the loose network of hd-CRC is the denser, corresponding to the gradually decreasing electrical conductivity (Figure 5d and Figure S8, Supporting Information). When the yield strength reaches 92.04 MPa, the electrical resistivity of hd-CRC can be reduced to 0.01 Ω cm. This compacted process of active electrode can determine its overall electrical conductivity, but excessive compaction will cause difficulties in ion diffusion and increase the resistance of electrolyte infiltration, further leading to poor rate performance (Figure 5e and Figure S9, Supporting Information). Importantly, the electrical conductivity of hd-CRC can reach 94.55 S cm⁻¹ at a compacted density of 1.09 $m^3 g^{-1}$. With the increase of yield strength, conductive particles can begin to contact each other to form a continuous conductive percolation network for promoting the rapid increase of electrical conductivity. According to the linear fitting curve, both electrical resistivity and yield strength of conductive agent can obey a power law above the percolation threshold (Figure 5f and Figure KSU). Compared with Super-C45, movement amplitude of hd-CRC can significantly expand with the increase of yield strength, indicating a low percolation threshold. Evidently, the synergistic effect of chemical stripping and capillary evaporation can effectively regulate the pore size distribution, the SSA, and pore volume.

For the practical applications of hd-CRC, symmetrical supercapacitors with $1 \le Et_4 NBF_4/AN$ were fabricated to explore the electrochemical properties of active electrode in the voltage range of 0–2.7 V. As shown in **Figure 6**a, AC impedance was used to explore its charge transfer resistance. In the high frequency region, the hd-CRC based supercapacitor exhibits a relatively small semi-

www.small-journal.com





Figure 4. Construction of conductive ramie carbon with different conductive networks. a,e,i) Schematically illustrating the conductive mechanism of high-amorphous conductive ramie carbon (ha-CRC), high-dense conductive ramie carbon (hd-CRC) and high-crystalline conductive ramie carbon (hc-CRC). b,f,j) Schematic diagram of storage of electrolyte ions and transmission of electrons. c,g,k) Representative TEM images of ha-CRC, hd-CRC, and hc-CRC. d,h,l) Pore size distribution of ha-CRC, hd-CRC.

circle and a corresponding equivalent series resistance of 0.75Ω , revealing the fast charge transfer capability. While in the low frequency region, the curve is close to 90° for reflecting the nearly ideal capacitance characteristics. CV curve result presents a regular rectangular shape for proving the fast charge transfer ability, and possess a relatively high retention rate of capacity at a scan rate of 2000 mV s⁻¹ (Figure 6b and Figure S11, Supporting Information). Further, GCD curve value demonstrates a high specific capacitance of 27.14 F g^{-1} and a relatively low *IR* drop of 0.475 V, indicative of the excellent rate performance (Figure 6c and Figure S12, Supporting Information). hd-CRC as conductive additive is conducive to improving the capacity and retention rate of supercapacitors from 75.92% to 82.87% (Figure 6d and Figure S13, Supporting Information). Especially, its volumetric capacity is 15.74 F cm⁻³, and the corresponding capacity improvement rate is up to 22.26% compared with NCRC based supercapacitor, evidently proving that highly dense hd-CRC as conductive additive could remarkably elevate the volume of active electrode after compaction (Figure 6e). Besides, multiple supercapacitors can obtain the prominent capacity or working voltage for practical application through series connection and parallel connection (Figure 6f,g). This hd-CRC as conductive additive presents a highly energy density of 15.53 Wh kg⁻¹ at 44.60 kW kg⁻¹ and 9.01 Wh L^{-1} at 25.87 kW L^{-1} , much better than of commercialized Super-C45 (10.11 Wh kg^{-1} at 38.60 kW kg^{-1} and 5.06 Wh

 L^{-1} at 19.30 kW L^{-1}), evidently illustrating the excellent energy storage behavior to solve the low volumetric energy density under the condition of high-power density (Figure 6h,i). In order to explore the cycle life of hd-CRC based supercapacitor, the retention rate of device remarkably reaches 75.93% after 50 000 cycles at a current density of 10 A g⁻¹, demonstrating the outstanding cycle stability (Figure 6j). The above results can further confirm that hd-CRC plays a vital role in improving the electrochemical performance and stability of electrode materials and supercapacitor devices.

To further evaluate the feasibility of hd-CRC in highlyvolumetric–performance supercapacitors, the active electrodes were developed with areal density of 10 mg cm⁻² as positive and negative electrodes to assemble the flexible supercapacitor by pulping, coating, dying electrode, compacting, tailoring electrode, and lamination (**Figure 7a** and Table S3, Supporting Information). As shown in Figure 7b, Super-C45 as conductive additive with low density of 0.16 cm³ g⁻¹ has a high liquid absorption, resulting in a large consumption of electrolyte. Therefore, hd-CRC with higher density of 0.47 cm³ g⁻¹ builds the efficient ion transport channels, and effectively reduces the amount of electrolyte. Adsorption and desorption curve presented the obvious hysteresis loop, which proved that the concentrated distribution of mesopores in the electrode could provide a place to realize the transmission and storage of electrolyte ions (Figure 7c). The

NANO · MICRO

www.small-journal.com

CIENCE NEWS



Figure 5. Intrinsic property of hd-CRC and Super-C45. a) Tap density. b) N_2 adsorption/desorption isotherms. c) Pore size distribution. d) Electrical conductivity as a function of yield strength. e) Compacted density as a function of electrical conductivity. f) Linear fitting curve based on power law.

average pore diameter of active electrode (2.14 nm) is much larger than the diameter of electrolyte ion, effectively reducing the ion transmission resistance. As shown in Figure 7d, pore volume of hd-CRC based electrode was about 0.55 cm³ g⁻¹ after compaction, and the SSA was 807.52 m² g⁻¹. As shown in Figure 7e, ESR of 301.99 F supercapacitor was only 3.93 m Ω , evidently demonstrating the low internal loss of device. Figure 7f presented the leakage current of hd-CRC based supercapacitor charged to 2.7 V at 0.25 A. Even if the capacity of supercapacitor is from 27.38 to 301.99 F, the corresponding leakage current is only expanded by 4.44 times for indicating a low self-discharge capability. Its CV curve presented a regular rectangular shape at a scan rate of 1 mV s⁻¹ for indicating the excellent double-layer capacitance (Figure 7g). GCD curve carried out constant current charging at a current of 5.48 A. When the target voltage reaches 2.7 V, the charging current of supercapacitor could drop to 0.01 A by adopting the constant voltage charging (Figure 7h and Figure S14, Supporting Information). Based on it, the retention rate of device remarkably reached 87.67% after 14 000 cycles at a current of 11.5 A, demonstrating the outstanding cycle stability (Figure S15, Supporting Information). Attractively, the device did not experience overcharging for demonstrating the excellent stability after 14 000 cycles. Finally, hd-CRC based supercapacitor could still successfully light up the parallel LED pattern by means of tapping (Figure 7i and Figure S16, Supporting Information).

The highly volumetric-performance of hd-CRC based supercapacitor is attributed to the outstandingly 3D conductive network formed between active substance and conductive agent, which can maintain the high compaction density and improve the conductivity of active electrode. First, capillary evaporation strategy regulates the capillary tension of cellulose molecules, further benefiting the densifying and ordering of cellulose structures. Second, the composition forms of C elements from the chemically-stripped ramies can orderly re-organize the C atoms and re-construct a large number of C=C bonds. In addition, hd-CRC with hGMCs effectively improves the space volume ratio of active electrode materials and obviously enhances the diffusion dynamics, synergistically promoting the cycle stability and rate performance of supercapacitor. More importantly, the capillary evaporation strategy can extremely extract the cellulose with complete crystal structure, preparing the high-dense conductive biomass carbon with hGMCs at a lower carbonization temperature.

3. Conclusion

In summary, an effective capillary evaporation strategy was proposed to build the hd-CRC with hGMCs, solving the rapid movement of π electrons. Utilizing this strategy, a large number of broken C–C bonds and C–H bonds from cellulose molecules would be re-organized and re-ordered to reconstruct substantial C=C bonds for the formation of hd-CRC with hGMCs. This capillary evaporation mechanism eventually leads to uniquely conductive biomass carbon, which can remarkably improve the intrinsic properties including electrical conductivity, SSA, pore volume, tap density, and compacted density. Specifically, hd-CRC as conductive additive structurally constructed a 3D conductive network toward the greatly-improved density of active electrode. A hd-CRC based super-capacitor presented the prominent power density of 9.01 Wh L⁻¹, corresponding to the energy density of 9.01 Wh L⁻¹

www.small-journal.com

ADVANCED SCIENCE NEWS __

www.advancedsciencenews.com

www.small-journal.com



Figure 6. Electrochemical performance of hd-CRC and Super-C45 based supercapacitors. a) AC impedance. b) CV curve at a scan rate of 2000 mV s⁻¹. c) GCD curve at a current density of 40 A g⁻¹. d) Curve of mass specific capacitance changing with current density. e) Curve of volumetric capacitance changing with current density. f) GCD curve at a current density of 1 A g⁻¹ and g) CV curve at a scan rate of 100 mV s⁻¹ for comparing the single supercapacitor, series supercapacitor, and parallel supercapacitor. h,i) Ragone plots.^[36–46] j) Curve of cycle life.

ADVANCED SCIENCE NEWS

www.advancedsciencenews.com



Figure 7. Electrochemical performance of hd-CRC based flexible supercapacitor. a) Manufacturing process. b) Electrolyte absorption of active electrode. c) N_2 adsorption/desorption isotherms. d) Pore size distribution. e) Equivalent series resistance of supercapacitor with different capacities. f) Leakage current of supercapacitor with different capacities. g) CV curve at 1 mV s⁻¹. h) GCD curve of constant current and constant voltage charging. i) Photo of green LEDs.

outperforming most AC-based supercapacitor with Super-C45 as conductive additive (5.06 Wh L^{-1} and 19.30 kW L^{-1}). This study clearly proves the effectiveness of hd-CRC in improving the electrochemical stability and volume performance, promoting the practical application of traditional AC electrode.

4. Experimental Section

Chemicals Reagent and Quantity: Concentrated sulfuric acid (98%, wt%), formic acid, hydrogen peroxide (30%, wt%), sodium hydroxide, and hydrochloric acid were acquired from Chengdu Kelong Chemicals Co., Ltd., China.

Preparation of Chemically Stripped Ramie: The chemically stripped ramie was synthesized by a mild chemical process. First, 50 g natural ramie was treated by water bath at the temperature (90 °C) for 2 h. Then, cooled ramie was dried in a vacuum oven at 100 °C for 24 h. Sequentially, 1500 mL formic acid, 300 mL H₂O₂, and 12 mL H₂SO₄ were successively added to the beaker, and stirred at 30 °C for 2 h to obtain the peroxyformic acid at 35 °C for 12 h. The obtained ramie precursors were treated with 0.5 m NaOH aqueous solution at 50 °C for 2 h. Finally, asprepared chemically stripped ramie was washed to neutral by deionized water, and dried for 24 h at the aimed temperature (70 °C).

Preparation of NCRC: The NCRC was synthesized by high-temperature pyrolysis. First, 500 g natural ramie treated with water bath was evenly placed in the quartz liner, and slowly pushed into the intermittent rotary furnace. Then, the natural ramie was heated to 1000 °C at a heating rate of $3 \,^{\circ}$ C min⁻¹ under argon atmosphere with a flow rate of 1.2 L min⁻¹. When the target temperature was reached, the ramie was kept warm for 2 h, and then naturally cooled to normal temperature. Sequentially, the obtained carbon treated with rough grinding was treated with 1 \times HCl solution for 6 h. Then, the NCRC was washed to neutral by a large amount of deionized water, and dried for 24 h at the aimed temperature (120 °C). Based on it, the above NCRC was further refined by wet grinding with the parameter of 350 r min⁻¹ and 12 h. Then, the as-prepared NCRC was washed by a large amount of deionized water, and dried for 24 h at the aimed temperature (120 °C). Finally, the obtained NCRC was heated to 500 °C for passivation treatment, further eliminating the impurity ions.

Preparation of hd-CRC: The hd-CRC was synthesized by hightemperature pyrolysis. First, 500 g chemically stripped ramie treated with capillary evaporation was evenly placed in the quartz liner, and slowly pushed into the intermittent rotary furnace. Then, the chemically stripped ramie was heated to different aimed temperatures (800, 900, 1000, 1100, and 1200 °C) at a heating rate of 3 °C min⁻¹ under argon atmosphere with a flow rate of 1.2 L min⁻¹. When the target temperature was reached, the ramie was kept warm for 2 h, and then naturally cooled to normal temperature. Sequentially, the obtained carbon after rough grinding was treated with 1 \bowtie HCl solution for 6 h. Then, the hd-CRC was washed to neutral by deionized water, and dried for 24 h at the aimed temperature (120 °C). Based on it, the above hd-CRC was further refined by wet grinding with the parameter of 350 r min⁻¹ and 12 h. Then, the as-prepared hd-CRC was washed by deionized water, and dried for 24 h at the aimed temperature (120 °C). Finally, the obtained hd-CRC was heated to 500 °C for passivation treatment, further eliminating the impurity ions.

Manufacturing Process of hd-CRC Based Supercapacitor: Electrode paste was prepared by adding the activated carbon (AC), hd-CRC, CMC (1 wt%), and SBR (50 wt%) to a certain amount of deionized water in a mass ratio of 85:10:1.2:3.8 through vacuum mixer. Then, the filtered slurry was evenly coated on the carbon-coated aluminum foil to obtain an active electrode with an areal density of 10 mg cm⁻². Subsequently, the electrode after drying and slicing was compacted to a density of 0.55 g cm⁻³. Then, the electrodes after cutting were assembled into different layers of flexible supercapacitors using the 1 m Et₄NBF₄/AN as electrolyte. Finally, electrochemical workstation and Sunway battery test system were used for electrochemical performance test at room temperature.

Characterization Methods: TEM and SEM characterized the morphology, composition, and structure of the obtained materials. XRD analyzed the phase, crystallinity, and crystal plane structure of the obtained materials. Raman spectroscopy characterized the ordering degree of graphitized carbon. XPS analyzed the element composition, contents, and bonding mode of the obtained materials. Nitrogen adsorption and desorption test characterized the SSA and pore structure of carbon materials. FTIR test determined the substance composition and molecular structure.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 51972277) and the Sichuan Science and Technology Program (No. 2018RZ0074). The authors are thankful to the Analytical and Testing Center of Southwest Jiaotong University for providing the SEM measurements.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

capillary evaporation, flexible package supercapacitors, high-dense conductive biomass carbon, highly graphitized microcrystals, volumetric energy density

> Received: April 20, 2023 Revised: May 30, 2023 Published online:

 Y. Sun, X. L. Shi, Y. L. Yang, G. Q. Suo, L. Zhang, S. Y. Lu, Z. G. Chen, Adv. Funct. Mater. 2022, 32, 2201584.

- Q. Wang, Y. Y. Chen, X. Jiang, N. A. X. Qiao, Y. H. Wang, H. B. Zhao, B. Pu, W. Q. Yang, *Energy Storage Mater.* 2022, 48, 164.
- [3] X. Zhang, J. Cheng, Z. Xiang, L. Cai, W. Lu, Carbon 2022, 187, 477.
- [4] F. Y. Liu, Q. Q. Wang, G. X. Zhai, H. X. Xiang, J. L. Zhou, C. Jia, L. P. Zhu, Q. L. Wu, M. F. Zhu, Nat. Commun. 2022, 13, 5755.
- [5] L. Luo, Y. L. Lan, Q. Q. Zhang, J. P. Deng, L. C. Luo, Q. Z. Zeng, H. L. Gao, W. G. Zhao, J. Energy Storage **2022**, 55, 105839.
- [6] H. Zheng, Q. P. Cao, M. N. Zhu, D. Xu, H. Y. Guo, Y. Li, J. H. Zhou, J. Mater. Chem. 2021, 9, 10120.
- [7] A. Al Rai, M. Yanilmaz, Cellulose 2021, 28, 5169;
- [8] X. M. Yuan, B. Zhu, J. K. Feng, C. G. Wang, X. Cai, R. M. Qin, Chem. Eng. J. 2021, 405, 126897.
- Q. Wang, F. Y. Liu, Z. Y. Jin, X. R. Qiao, H. C. Huang, X. Chu, D. Xiong, H. T. Zhang, Y. Liu, W. Q. Yang, *Adv. Funct. Mater.* 2020, *30*, 2002580.
- [10] S. M. Ji, A. Kumar, Polymers 2022, 14, 169.
- [11] J. J. Chen, J. X. Xie, C. Q. Jia, C. Y. Song, J. Hu, H. L. Li, Chem. Eng. J. 2022, 450, 137938.
- [12] K. Chen, Z. J. He, Z. H. Liu, A. J. Ragauskas, B. Z. Li, Y. J. Yuan, Chem-SusChem 2022, 15, 202201284.
- [13] Z. L. Zhang, F. F. Li, J. C. Chen, G. H. Yang, X. X. Ji, Z. J. Tian, B. B. Wang, L. Zhang, L. Lucia, *Front. Bioeng. Biotechnol.* **2022**, *10*, 1030944.
- [14] X. Z. Shi, S. Zhang, X. C. Chen, T. Tang, E. Mijowska, Carbon 2020, 157, 55.
- [15] X. L. Ma, X. Y. Song, Z. Q. Yu, S. P. Li, X. J. Wang, L. Zhao, L. Zhao, Z. H. Xiao, C. L. Qi, G. Q. Ning, J. S. Gao, *Carbon* **2019**, *149*, 646.
- [16] S. Y. Li, L. Zhang, L. X. Zhang, Y. Q. Guo, X. C. Chen, R. Holze, T. Tang, New J. Chem. 2021, 45, 16011.
- [17] D. X. Guo, X. M. Song, L. C. Tan, H. Y. Ma, H. J. Pang, X. M. Wang, L. L. Zhang, ACS Sustainable Chem. Eng. 2019, 7, 2803.
- [18] X. G. Liu, C. D. Ma, Y. L. Wen, X. C. Chen, X. Zhao, T. Tang, R. Holze, E. Mijowska, *Carbon* **2021**, *171*, 819.
- [19] D. W. Chu, F. B. Li, X. M. Song, H. Y. Ma, L. C. Tan, H. J. Pang, X. M. Wang, D. X. Guo, B. X. Xiao, J. Colloid Interface Sci. 2020, 568, 130.
- [20] Z. Bo, X. N. Cheng, H. C. Yang, X. Z. Guo, J. H. Yan, K. F. Cen, Z. J. Han, L. M. Dai, *Adv. Energy Mater.* **2022**, *12*, 2103394.
- [21] S. Kane, A. Storer, W. Xu, C. Ryan, N. P. Stadie, ACS Sustainable Chem. Eng. 2022, 10, 12226.
- [22] M. R. Snowdon, A. K. Mohanty, M. Misra, ACS Sustainable Chem. Eng. 2014, 2, 1257.
- [23] W. J. Sagues, J. Yang, N. Monroe, S. D. Han, T. Vinzant, M. Yung, H. Jameel, M. Nimlos, S. Park, *Green Chem.* 2020, 22, 7093.
- [24] C. Y. Zhou, X. Z. Gong, Z. Wang, J. H. Liu, *Electrochim. Acta* 2022, 414, 140184.
- [25] Q. Wang, Y. H. Zhou, X. Zhao, K. Chen, B. N. Gu, T. Yang, H. T. Zhang, W. Q. Yang, J. Chen, *Nano Today* **2021**, *36*, 101033.
- [26] C. E. Morstein, A. Klemenz, M. Dienwiebel, M. Moseler, Nat. Commun. 2022, 13, 5958.
- [27] M. S. Khosrowshahi, M. A. Abdol, H. Mashhadimoslem, E. Khakpour, H. B. M. Emrooz, S. Sadeghzadeh, A. Ghaemi, *Sci. Rep.* 2022, *12*, 8917.
- [28] C. X. Wang, R. G. Zou, M. Qian, X. Kong, E. G. Huo, X. N. Lin, L. Wang, X. S. Zhang, R. Ruan, H. W. Lei, *Bioresour. Technol.* 2022, 355, 127251.
- [29] T. R. Sarker, F. Pattnaik, S. Nanda, A. K. Dalai, V. Meda, S. Naik, *Chemosphere* 2021, 284, 131372.
- [30] D. D. Perez, M. G. H. Terrones, S. Grelier, A. Nourmamode, A. Castellan, R. Ruggiero, A. E. H. Machado, J. Wood Chem. Technol. 1998, 18, 333.
- [31] Z. H. Li, C. J. Chen, H. Xie, Y. Yao, X. Zhang, A. Brozena, J. G. Li, Y. Ding, X. P. Zhao, M. Hong, H. Y. Qiao, L. M. Smith, X. J. Pan, R. Briber, S. Q. Shi, L. B. Hu, *Nat. Sustain.* **2022**, *5*, 235.
- [32] Y. C. Peng, D. J. Gardner, Y. S. Han, Cellulose 2012, 19, 91.

ADVANCED SCIENCE NEWS

www.advancedsciencenews.com

- [33] M. Usselmann, J. Bansmann, A. J. C. Kuehne, Adv. Mater. 2022, 35, 2208484.
- [34] K. Nanaji, A. Nirogi, P. Srinivas, S. Anandan, R. Vijay, R. N. Bathe, M. Pramanik, K. Narayan, B. Ravi, T. N. Rao, J. Energy Storage 2022, 55, 105650.
- [35] M. Dvoyashkin, D. Leistenschneider, J. D. Evans, M. Sander, L. Borchardt, Adv. Energy Mater. 2021, 11, 2100700.
- [36] G. P. Hao, A. H. Lu, W. Dong, Z. Y. Jin, X. Q. Zhang, J. T. Zhang, W. C. Li, Adv. Energy Mater. 2013, 3, 1421.
- [37] T. C. Mendes, C. L. Xiao, F. L. Zhou, H. T. Li, G. P. Knowles, M. Hilder, A. Somers, P. C. Howlett, D. R. MacFarlane, ACS Appl. Mater. Interfaces 2016, 8, 35243.
- [38] P. Cheng, S. Y. Gao, P. Y. Zang, X. F. Yang, Y. L. Bai, H. Xu, Z. H. Liu, Z. B. Lei, *Carbon* **2015**, *93*, 315.

- [39] F. Markoulidis, C. Lei, C. Lekakou, D. Duff, S. Khalil, B. Martorana, I. Cannavaro, *Carbon* 2014, 68, 58.
- [40] G. A. Ferrero, A. B. Fuertes, M. Sevilla, J. Mater. Chem. 2015, 3, 2914.
- [41] M. Sevilla, A. B. Fuertes, ACS Nano 2014, 8, 5069.
- [42] A. M. P. Sakita, R. Della Noce, P. L. Gastelois, W. A. A. Macedo, R. L. Lavall, Chem. Eng. J. 2022, 427, 131731.
- [43] M. Zhang, Z. H. Sun, T. F. Zhang, B. Qin, D. Sui, Y. Q. Xie, Y. F. Ma, Y. S. Chen, J. Mater. Chem. 2017, 5, 21757.
- [44] J. Pang, W. F. Zhang, J. L. Zhang, G. P. Cao, M. F. Han, Y. S. Yang, Green Chem. 2017, 19, 3916.
- [45] L. N. Ma, Z. J. Bi, W. Zhang, Z. H. Zhang, Y. Xiao, H. J. Niu, Y. D. Huang, ACS Appl. Mater. Interfaces 2020, 12, 46170.
- [46] W. J. Ma, M. Li, X. Zhou, J. H. Li, Y. M. Dong, M. F. Zhu, ACS Appl. Mater. Interfaces 2019, 11, 9283.