



Scalable and sustainable synthesis of carbon microspheres via a purification-free strategy for sodium-ion capacitors



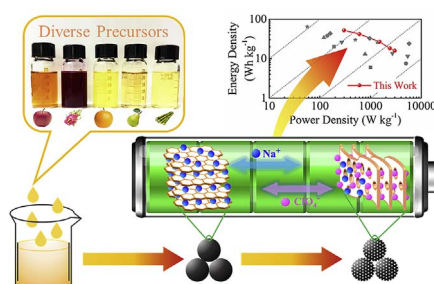
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HIGHLIGHTS

- Scalable purification-free strategy is used to obtain non-graphitic carbon spheres.
- A variety of sap-based carbon precursors are available with high sustainability.
- Ultra-stable Na-ion capacitor anodes retain 99.0% of capacity after 10000 cycles.
- Full-cell Na-ion capacitors are assembled based on the same initial precursors.
- Such capacitors deliver 52.2 Wh kg^{-1} , and show excellent reversibility.

GRAPHICAL ABSTRACT



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ABSTRACT

Sodium-based energy storage receives a great deal of interest due to the virtually inexhaustible sodium reserve, while the scalable and sustainable strategies to synthesize carbon-based materials with suitable interlayer spaces and large sodium storage capacities are yet to be fully investigated. Carbon microspheres, with regular geometry, non-graphitic characteristic, and stable nature are promising candidates, yet the synthetic methods are usually complex and energy consuming. In this regard, we report a scalable purification-free strategy to synthesize carbon microspheres directly from 5 species of fresh juice. As-synthesized carbon microspheres exhibit dilated interlayer distance of 0.375 nm and facilitate Na^+ uptake and release. For example, such carbon microsphere anodes have a specific capacity of 183.9 mAh g^{-1} at 50 mA g^{-1} and exhibit ultra-stability (99.0% capacity retention) after 10000 cycles. Moreover, via facile activation, highly porous carbon microsphere cathodes are fabricated and show much higher energy density at high rate than commercial activated carbon. Coupling the compelling anodes and cathodes above, novel sodium-ion capacitors show the high working potential up to 4.0 V, deliver a maximum energy density of 52.2 Wh kg^{-1} , and exhibit an acceptable capacity retention of 85.7% after 2000 cycles.

1. Introduction

With extensive emphasis on distributed electrical systems, energy storage devices are becoming increasingly important, among which, supercapacitors, owing to their swift frequency response, high power

rate, and durable cycle life, are of special interest to researchers [1–4]. Among all the electrode materials for supercapacitors, carbon materials are widely used, because of their abundance in reserve, high chemical stability, excellent electrical conductivity, as well as tunable pore structure and performance [5–11]. However, limited energy density of

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traditional carbon-based electric double-layer capacitors hinders their practical applications. Thus, an emerging strategy for advanced carbon-based energy storage devices is to construct hybrid ion capacitors that are capable of spanning the energy and power divide by coupling the intercalative anodes of batteries and adsorptive cathodes of capacitors [12–18]. Currently, lithium-based hybrid ion capacitors have been widely studied, but the shortage of lithium source has become the major challenge for further development [19,20]. By contrast, the sodium reserve is virtually inexhaustible on the earth and hence of low-cost [21]. Therefore, sodium-ion capacitors (SICs) are currently attracting substantial attention and considered as the most promising alternative compared to the analogous lithium-based technologies.

Graphite, the typical anode materials used in lithium-based energy storage devices, exhibits unsatisfactory Na^+ accommodation by intercalation due to its limited interlayer space (0.335 nm), and hence other carbon alternatives need to be further explored as high-performance anodes of SICs [13,19,20]. Carbon microspheres (CSs) featured with regular and sharp-edge-free geometry, good liquidity, and high stability have shown various of applications, including adsorption of gas and vapors [7,22], catalysis [23–25], and electrochemical energy storage [22,24,25]. Hence, they receive extensive attention as a versatile form of carbon. Especially in energy-storage field, non-graphitic CSs with heteroatom doping can open up the interlayer space to facilitate intercalation and deintercalation of Na^+ [13,19,20]. Therefore, CSs are considered as a promising alternative to replace graphite for effective sodium storage. Currently, a wide variety of synthetic methods have been used to design and fabricate CSs. Among them, hard template method has been widely employed because the structures and morphologies of CSs can be precisely controlled, yet the procedures are tedious and time-consuming, with harsh chemicals (e.g., HF) usually used as template removal agents [7,22,26]. Compared to hard template method, soft template method simplifies the steps, while fabrication and cross-linking are even difficult due to weak interactions between carbon sources and soft templates [26,27]. Besides, extended Stöber method also bears deficiencies by using toxic phenol formaldehyde resin as the typical carbon source in a non-aqueous solution, which is unfavorable for sustainable synthesis [28].

Compared to all the methods above, hydrothermal treatment has the advantages of simplicity, mild synthetic condition, and possible acceleration by microwave-assisted strategy, thus regarded as an effective, scalable, and sustainable approach to synthesize CSs [25,28–31]. A wide variety of carbon sources can be used, but unfortunately, most of the reports only select limited species of purified saccharides (e.g., glucose, xylose, and starch) as the carbon sources [29–31], which requires additional efforts and energy input before pure saccharides are obtained, e.g., from sugarcane and sugar sweets [32], starch [33], and cellulose [34]. In this regard, we believe that if abundant fresh juice without purification is used directly for preparing CSs, the synthetic process can be simplified, more scalable and environmentally benign.

Herein, we report a scalable purification-free strategy to synthesize CSs directly from various kinds of fresh juice by hydrothermal method. The large annual yield of fruits and high juice content of most fruits make such carbon sources easily accessible and hence inexpensive. Further based on the reported mechanism that CSs can be formed by hydrothermally treating (purified) sugar solutions [29], we believe that our strategy can be readily extended to any sugar containing saps. When as-synthesized CSs are used as anodes of SICs, a specific capacity of 183.9 mAh g^{-1} at 50 mA g^{-1} can be achieved. Capacity retention of 99.0% after 10000 charge and discharge cycles further reveals the stable characteristic of such CSs. Then, by activating CSs and employing them as cathode materials, we figure out that activated CS cathodes show a specific capacity of 67.5 mAh g^{-1} (0.1 A g^{-1}) with a capacity retention of 60.3% (5.0 A g^{-1}). Rate capability of such activated CSs is much superior to that of commercial activated carbon. The cathodes also retain 90.8% of the initial capacity after 2000 charge and discharge

cycles, showing excellent stability. Furthermore, we assemble these CS anodes and activated CS cathodes into full-cell SICs. Optimized full-cell SICs can deliver an energy density of 52.2 Wh kg^{-1} at a power density of 300 W kg^{-1} , with a capacity retention of 85.7% after 2000 charge and discharge cycles at 1.0 A g^{-1} , which is comparable to many other SICs.

2. Experimental section

2.1. Materials and reagents

All the fruits (i.e., apples, dragon fruits, oranges, and pears) were purchased from a local supermarket (Hong Kong, China). Juice was extracted using a commercial blender (Kenwood Blend-X Mini, 350 W, UK). Sugarcane juice was purchased from a local fresh juice bar (Hong Kong, China). D-(+)-glucose (AR) was purchased from Aladdin Reagent Co., Ltd (China). KOH (AR, 90%) was purchased from Aladdin Reagent Co., Ltd (China). Sodium metal (Na oiled sticks, 99.5%) was purchased from J&K Scientific (China). Commercial activated carbon (CAC) was purchased from Shanghai Heda Carbon Materials Co., Ltd (China).

2.2. Synthesis of carbon microspheres (CSs)

Fruits were first put into a commercial blender to extract fresh juice. A minimum amount of water was added according to the user manual of the blender. As-obtained juice was then centrifuged at a moderate speed (6000 rpm) for 5 min to further remove minor solid substances. No further physical or chemical purification procedures were required. Sugarcane juice was used as purchased. 32 mL of fresh juice was then loaded into a 40 mL Teflon-lined stainless-steel autoclave and hydrothermally treated at $180 \text{ }^\circ\text{C}$ for 6 h. Afterwards, precipitates were collected, rinsed with deionized water, and dried at $60 \text{ }^\circ\text{C}$ in an electrical oven. The collected brown solids were then grounded, loaded into an Al_2O_3 boat, and pyrolyzed in a tube furnace at $800 \text{ }^\circ\text{C}$ for 2 h (Ar atmosphere, Ar flow rate: 40 standard cubic centimeter per minute (sccm), ramping rate: $5 \text{ }^\circ\text{C min}^{-1}$). The procedures for fabricating CSs from spoiled orange juice were the same as above, except that fresh orange juice was first stored in ambient condition ($20\text{--}25 \text{ }^\circ\text{C}$) for 2 weeks. For comparison, glucose was also treated with the above procedures for CSs. In brief, 7.2 g of glucose was added into the PTFE autoclave and dissolved in water completely before hydrothermal treatment.

2.3. Synthesis of activated CSs

Typically, 0.5 g of CSs was mixed with 3 g KOH (KOH:C = 6:1, w/w). Mixtures were loaded into the Al_2O_3 boat again and activated at $800 \text{ }^\circ\text{C}$ for 2 h. The resultant black solids were immersed in 1 M HCl solution and magnetically stirred overnight. Then, the products were filtered and washed with deionized water until a pH value of 7 was reached. Finally, the obtained activated CSs were dried at $60 \text{ }^\circ\text{C}$ in an electrical oven.

2.4. Materials characterization

Scanning electron microscopy (SEM) was carried out using a JEOL JSM-7800F microscope. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were used on a field emission Tecnaï F20 microscope. Samples were also inspected by powder X-ray diffraction (XRD) and ex-situ XRD using a SmartLab diffractometer (monochromatic $\text{Cu K}\alpha 1$ radiation, $\lambda = 1.54059 \text{ \AA}$, 40 kV, 30 mA). For ex-situ XRD, disassembled electrodes were stored in the Ar-filled containers until the beginning of the tests. Raman spectroscopy were recorded using a micro-Raman spectroscopy (JYHR800, $\lambda = 532 \text{ nm}$). X-ray photoelectron spectroscopy (XPS) was performed on a Perkin-Elmer PHI-5702 multifunctional photoelectron spectrometer (Physical

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