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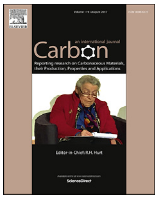

Unusual interconnected graphitized carbon nanosheets as the electrode of high-rate ionic liquid-based supercapacitor

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ABSTRACT

A type of unusual interconnected graphitized carbon nanosheets (GCNS) was fabricated from biomass waste, *i.e.*, inner shaddock skins using a facile combined method of simultaneous carbonization-activation and post-vacuum-annealing processes. The obtained GCNS has an optimized integration of a cage-like high-aspect-ratio nanosheet structure (~8 nm thickness), a large surface area of 2327 $m^2\ g^{-1}$ and hierarchical meso/micropore systems (82.3% mesopore volume). Given the effect of post-vacuum-annealing process, enhanced graphitization degree and excellent electronic conductivity (7.9 S cm^{-1}) were obtained for the GCNS. The enhanced graphitization degree not only effectively improves electronic/ionic-transport kinetics in favor of rate capability but also prevents electrolyte degradation thus benefitting cyclic life. The ionic liquid-based supercapacitors assembled with symmetric GCNS electrodes exhibited an ultrahigh rate capability of 87% at current density of 100 A g^{-1} (holding 132 F g^{-1}) and a long cyclic life of 97.6% capacitance retention after 10,000 cycles. The excellent rate capability resulted in an integrated high energy-power property at an energy density of 56 Wh kg^{-1} (29.2 Wh L^{-1}), corresponding to a power density of 93 kW kg^{-1} (48.4 kW L^{-1}).

1. Introduction

Supercapacitors or electrochemical double layer capacitors, assembled by carbon (*e.g.*, graphene, activated carbons and carbon nanosheets) electrodes and ionic liquid (IL) electrolytes, have been dramatically developed during the past years [1–11]. This development is mainly ascribed to the integrated effects of carbon electrodes and IL electrolytes. The large specific surface area and high porosity of carbonaceous nanomaterials can be in favor of charge storage [12,13]; furthermore, the high electrochemical stability, good ionic conductivity and non-flammability of ILs can provide large operating voltage window and wide operating temperature range even at an extreme aerospace environment [11,14]. Such advantages make these supercapacitors suitable for the power sources of portable electronics, uninterruptible power supplies, hybrid electric vehicles, regenerative braking systems, grid applications, *etc.* [7,10,15].

In principle, the energy storage mechanism of supercapacitors is the non-Faradaic electrostatic sorption on the solid-fluid interface of electrode-electrolyte, which leads to a limited energy storage capacity. Thus, many concept designs and experimental strategies were explored to enhance the energy density of supercapacitors without sacrificing originally high power density and long cyclic life. These are based on the energy density (E, equaling to $\frac{1}{2}CV^2$) that is linear with the capacitance (C) and quadratic with the voltage window (V). For example, first, optimizing geometric parameters of carbon electrodes with a high specific surface area and matched pore size for electrolyte ion can generate sufficient interface charge storage for high double-layer capacitance [16]. Second, enhancing graphitization degree of carbon materials not only possibly improves the electrical conductivity to accelerate charge transfer in favor of a high rate performance, but may also increase the charge carrier density to boost charge screening at electrode-electrolyte interface resulting in high quantum capacitance [17]. Third, formation of novel IL electrolyte systems to balance the charge capacity of symmetric electrodes can expand the operating voltage window and increase the ability to screen charges for electro-adsorbing more electrolyte ions [18].

Regarding to the advanced supercapacitor electrode materials, two-dimensional (2D) carbonaceous material with abundant sp^2 hybridization and/or heteroatom doping is very promising because

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of its short ionic transport pathways and rich interface active sites compared with that of the activated carbon particles [4,19,20]. For example, as typical 2D carbonaceous materials, graphenes and MXenes have been intensively developed as supercapacitor electrodes with excellent capacitive performances. However, manufacturing these 2D carbonaceous materials is a complex process and requires high-cost feedstock. Currently, some 2D graphene-like carbon nanosheets have been prepared using eco-friendly and low-cost methods from waste biomass, such as silk [8], shrimp shells [11], hemp [4], gelatin [21], cornstalk [22] and coffee grounds [9]. These sustainable carbon nanosheets have thin thickness of less than 30 nm and high specific surface areas, which can potentially substitute the graphene for supercapacitor electrodes used. This possibility opens a door to create advanced carbon nanosheet electrodes for high-performance supercapacitors. However, most of the biomass-derived carbon nanosheet electrodes exhibit low-rate capability in organic and/or IL electrolyte systems, leading to inferior energy retention at high power output. This result mismatches the demand for devices requiring both high energy and high power.

In this study, a type of unusual interconnected graphitized carbon nanosheet (GCNS) material was prepared from waste biomass, *i.e.*, inner shaddock skins (ISSs), by using a facile combined method of simultaneous carbonization-activation and post-vacuum-annealing processes. The as-obtained GCNS presents good integration of a cage-like high-aspect-ratio nanosheet structure, hierarchical meso/micropore systems, large surface area and excellent electronic conductivity, which is different from the usual biomass-based activated carbons. These integrated characteristics render an excellent electrochemical performance for GCNS electrodes in the IL-based supercapacitor assembly.

2. Experimental

2.1. Materials

The inner shaddock skins (ISSs) were obtained from the shaddocks (citrus grandis) grown in the south of China. The N,N-dimethylacetylamide (DMAC), zinc chloride ($ZnCl_2$), ferric trichloride ($FeCl_3$) and hydrochloric acid (HCl) were purchased from Beijing Chemical Works. 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMI TFSI) and 1-ethyl-3-methy-limidazolium tetrafluoroborate (EMI BF_4) were purchased from Sigma-Aldrich. All reagents used are analytically pure.

2.2. GCNS fabrication

The GCNS materials were synthesized as follows. The ISSs were firstly rinsed with distilled water and then dried. The dry ISSs were milled into powders in a hammer mill and then the powders underwent ultrasound-assisted pretreatment in DMAC. The suspension was vacuum-filtered, washed with ethanol and dried at 50 °C. The pretreated ISSs powders were mixed with $ZnCl_2$ by a mass ratio of 1:2 (ISS:$ZnCl_2$), and then put into 3 M $FeCl_3$ solution at a solid loading of 5 wt.% (a mass ratio of the ISSs to the $FeCl_3$ solution). The mixtures were continuously treated by ultrasonic for 3 h and then were dried thoroughly at 80 °C in a conventional oven. The pretreated carbon precursors were carbonized at 900 °C for 2 h with a ramp rate of 2 °C min^{-1} in a tubular furnace under Ar flow of 100 mL min^{-1}. The resulting dark char was washed with 1 M HCl solution to remove the inorganic impurities, then rinsed several times with deionized water to pH around 7 and dried at 110 °C for 10 h. The obtained material was denoted as CNS, and the yield of CNS was 28.2 wt.% based on the weight of dry ISSs powders. Then, the CNS underwent a post-vacuum-annealing in a tubular furnace under about 0.1 Pa at 1200 °C for 1 h, and the final product was obtained and named as GCNS. The control samples of GCNS-1 and GCNS-2 were prepared under the same procedures used to prepare the GCNS except for the different vacuum-annealing temperatures at 1000 and 1400 °C, respectively. The carbon yield was 7.9 wt.% for GCNS, 13.7 wt.% for GCNS-1 and 3.4 wt.% for GCNS-2, respectively, based on the weight of dry ISSs powders.

2.3. Characterization

Field emission scanning electron microscopy (FESEM) was carried out on the microscope S-3400N, Hitachi. Field emission transmission electron microscopy (FETEM) was examined on the JEM2100F, JEOL. X-ray diffraction (XRD) patterns were obtained on the X-6000, Shimadzu, using Cu Kα radiation at 40 kV with 2θ steps of 0.2°. Raman spectra were determined on the spectrometer LabRAM, HR800, at a laser wavelength of 514 nm. The chemical compositions were measured on X-ray photoelectron spectroscopy (XPS) of Escalab 250, Thermo. The electrical conductivity was tested by a four-point probe method on the Jandel, RM3 with a pin-distance of about 1 mm. The powder samples were pressed at room temperature between two plungers into a hollow stainless-steel cylinder at a pressure of 15 MPa for 30 s. The obtained disc-like samples with a diameter of 13 mm and a thickness of 0.8 mm, were measured at three different positions. The average values were acquired within an error range of $\pm 1\%$. N_2 adsorption-desorption isotherms were obtained on the Quantachrome Instrument to measure the specific surface areas and pore size distributions of samples, based on the multipoint Brunauer-Emmett-Teller (BET) and non-local Density Functional Theory (NLDFT) model using silt model, respectively.

2.4. Electrochemical testing

Two-electrode symmetrical cells were used to characterize the supercapacitive performances of our samples. The electrodes were prepared by pasting a slurry including 95 wt.% GCNS and 5 wt.% polyvinylidene difluoride (PVDF) binder without conductive additive onto the current collector of conducting carbon-coated aluminium foils (MTI Technologies). The as-prepared electrodes were dried at 100 °C for 12 h in vacuum oven and then were pressed at 10 MPa with a thickness of ~95 μm. The final mass loading on one electrode is around 5 mg cm^{-2} with a packing electrode density of 0.53 g cm^{-3}. A glass-fiber membrane (Whatman) was used as the separator, and an IL mixture of EMI TFSI and EMI BF_4 with volume ratio of 80:20 was used as the electrolyte. Finally, the symmetrical cells were assembled in an argon-filled glove box. For the symmetrical cells, the cyclic voltammetry (CV) curves, galvanostatic charge/discharge voltage profiles and electrochemical impedance spectroscopies were measured on a CHI660D electrochemical workstation. The specific capacitance C (F g^{-1}) was calculated from the upper part of discharge curves after voltage drops, according to $C = 2I/[(dV/dt)m]$ where I (A) is the discharge current, dV/dt is the slope of discharge curves in the range of V_{max} to $V_{max}/2$ and m (g) is the mass of active electrode material of one electrode. The energy density E (Wh kg^{-1}) and power density P (W kg^{-1}) were calculated from $E = CV^2/(8 \times 3.6)$ and $P = E/t$, respectively, where V (V) is the discharge voltage and t (h) is discharge time.

3. Results and discussion

3.1. Physicochemical characterization

Fig. 1 highlights the morphology characterization of the GCNS.