



Rational synthesis of porous carbon nanocages and their potential application in high rate supercapacitors

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ABSTRACT

Exploration of carbon nanoarchitectures with lower cost and excellent rate capability is of great importance, however, still remains a significant challenge. In the present work, a facile procedure for the fabrication of porous carbon nanocages (PCNCs) with a superior rate capability for supercapacitors has been developed. This approach is based on directly carbonization of sodium polyacrylate and subsequently chemical etching through a simple immersing-filtration-activation process. The extraordinary structures and morphologies of PCNCs has lots of structural advantages for supercapacitor applications. The supercapacitor assembled with the optimized sample can deliver a large specific capacitance (161 F/g at 1 A/g), superior rate capability (capacitance retention as high as 77.6% at 30 A/g), tiny IR drop (0.407 V at 30 A/g). Furthermore, in view of the wide working voltage (2.7 V) and excellent rate capability, the energy densities can retain at 30.2 Wh/kg at a large power density of 20.3625 kW/kg. Remarkably, the as-assembled supercapacitor can light 11 red light-emitting diodes (LED, 1.5 V) in parallel highlighting its enormous potential for practical applications.

1. Introduction

Nanocarbon-based supercapacitors, as a highly promising candidate for next generation energy storage devices, have attracted tremendous attention in view of their attractive advantages, such as ultrahigh power density, ultralong cycle life and outstanding reliability [1–6]. However, the energy density of most commercially available supercapacitors (5–10 Wh/kg) is still substantially lower than that of lithium-ion batteries that does not meet the ever-growing energy demands for advanced energy storage and conversion systems [7–12]. Therefore, developing advanced supercapacitors with high energy density without compromising their power density and cycle life is receiving considerable attention, and has become an essential part in the process design and exploit of various types of innovative electrode materials.

Given that the energy density of a supercapacitor is proportional to the specific capacitance of electrode and square of the operating voltage, intensive efforts have been devoted to exploring novel electrode materials with large specific capacitances and non-aqueous electrolytes with wide operating voltages (larger than 2 V) [8,13–17]. Generally, activated carbon based supercapacitors in organic electrolyte is very suitable for commercial applications because of the proper integrated the large specific surface area, cost-effective and excellent chemical stability of the electrode materials, and the meanwhile large decomposition voltage to boost the energy density [18,19]. Nevertheless, the

specific capacitance decreases dramatically at high rate mainly due to great increased resistance for larger size of electrolyte ions transport through the narrow microspore channels, and therefore the insufficient electrochemical accessible surface area [20,21]. Therefore, various carbon-based materials, such as carbon onions [22], carbide-derived carbons [23], graphene [24,25], hierarchical carbons [26], carbon nanocages (CNCs) and carbon nanotube [27], have been development aiming to improve the electrochemical performance especially rate capability. Particularly, CNCs, combining hollow cores, thin-walled graphitizing shells, and large accessible specific surface area, have been widely demonstrated to be the most promising candidates, where the unique architecture can not only minimize the diffusion distances to the interior surfaces but also reduce the diffusion resistance of ions, and consequently increase the electroactive surface area for ion transport/charge storage [28–31]. For instance, Hu and coworkers developed a facile in situ MgO template method for the synthesis of CNCs, and the optimized product shows large specific capacitance in the wide range of charging-discharging densities due to the large specific surface area, good mesoporosity and regular structure [31]. Sevilla's research group developing a novel nanocasting approach based on silica particles as a template for the synthesis of N-doped CNCs [29]. Electrochemical study proving that the N-doped CNCs displays excellent capacitive performance in aqueous and organic electrolytes due to its unique morphology. The existing methodologies for the preparation of CNCs,

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however, suffer from various issues, such as the lack of effective control of the microstructures, complicated and time-consuming procedures, and expensive and hazard raw materials.

Herein, we report an alternative approach that can address most of these concerns. In our approach, CNCs can be obtained by directly carbonization of sodium polyacrylate while the abundant micro and mesopores can be further introduced through an additional chemical activation process with KOH. As far as we know, there are few reports on preparation of carbon nanocages morphology by a template-free method. Particularly, the extraordinary structures and morphologies of PCNCs has lots of structural advantages made its very attractive electrode material for supercapacitors in organic electrolyte. Firstly, the central macroporous core can act as ion buffering reservoirs for the electrolyte solution to short the transport distance to the interior pores, thereby facilitating the ions diffusion during the charge-discharge process especially at high rate [32]. Secondly, thin-walled porous shells can provide highways for ions and electrons that ensuring good power handling capability [31]. Thirdly, the large amount of micro and mesopores can offer sufficient adsorption sites for electrolyte ion to enhance the electric double-layer capacitance [29]. Last but not the least, considering the easy-availability of the raw materials and feasible synthetic process, this facile and cost-effective method presented here is a very promising way toward CNCs for advanced supercapacitor applications. The optimized sample presents very attractive electrodes for organic electrolyte supercapacitors, including large specific capacitance (161 F/g at 1 A/g), superior rate capability (retention of 77.6% from 1 A/g to 30 A/g), smaller IR drop (0.407 V at 30 A/g). Moreover, benefiting from the excellent rate capability and wide working voltage (as large as 2.7 V), the energy density can reach to 40.7 Wh/kg at the power density of 0.675 kW/kg, and still maintained at 30.2 Wh/kg at an ultrahigh power density of 23.625 kW/kg, demonstrating the great potential for bridging the energy gap between electrolytic capacitors and batteries.

2. Experimental

2.1. Chemicals

In the present experiment, all the chemicals were purchased from Guoyao Chemical Reagent Co., Ltd. (Shanghai, China) without any further purification. Deionized water was used throughout the experiment.

2.2. Preparation of CNCs

In a typical synthetic procedure, 10 g of sodium polyacrylate was placed in a corundum boat in a horizontal tube furnace under Ar atmosphere at 500 °C for 1 h with a heating rate of 5 °C/min. The black products were collected, and neutralized with diluted HCl, then washed with abundant deionized water until the filtrate became neutral. Finally, the product was dried at 80 °C for several hours, and the yield was about 12%.

2.3. Preparation of PCNCs

Typically, 1 g of the as-obtained CNCs were immersed in 50 mL of KOH solution at different concentrations (3, 4, 5 and 6 M) for 12 h at ambient conditions. Afterwards, the extra KOH solution was removed by vacuum filtration and the samples were dried at 80 °C for 12 h, and then pyrolysis in tubular furnace at 800 °C for 1 h with a heating rate of 5 °C/min under argon flow. The solid residues were firstly neutralized with diluted HCl solution and then repeatedly washed with deionized water to remove any impurities. Finally, the chemical activated samples were dried at 80 °C in a vacuum oven overnight.

These activated carbon nanocages were labeled as PCNCX, X being the concentration of KOH solution. The obtained weight yields for

PCNC3, PCNC4, PCNC5 and PCNC6 were about 0.45, 0.33, 0.21 and 0.12 g, respectively.

2.4. Material characterization

The morphologies and microstructures of the samples were examined by scanning electron microscope (SEM, Zeiss Supra55) and transmission electron microscope (TEM, JEM-2100F, operating at 200 kV). The crystalline structures of the samples were evaluated by X-ray diffraction (XRD) analysis, which was recorded on a Shimadzu X-ray 6000 diffractometer using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) as an X-ray source. Raman spectra were performed with an inVia Raman spectrometer (Renishaw, England) with an excitation laser wavelength of 532 nm. The BET surface areas (S_{BET}) and pore size distributions of the samples were recorded by nitrogen adsorption-desorption isotherms at 77 K on a Micromeritics porosity analyzer (Micromeritics Instrument Corp. ASAP2020). The surface area was calculated according to the Brunauer-Emmett-Teller (BET) method and pore-size distributions were estimated from the nonlocal density functional theory (DFT). The surface elemental compositions and status were analyzed by the X-ray photoelectron spectroscopy (XPS, X-ray monochromatisation, Thermo Scientific) with Al K α as the radiation source. The binding energy was corrected by the C 1s line at 284.8 eV.

2.5. Electrochemical measurements

All the electrochemical measurements were performed on a CHI 660E electrochemical workstation (Shanghai Chenhua, China) at room temperature. Electrodes were prepared by mixing 85 wt% of the porous carbon samples with 10 wt% of conductive carbon black (Super P) and 5 wt% of Poly(tetrafluoroethylene) (PTFE) in ethanol to form a sticky slurry. The mixture was then rolled into a carbon film with thickness of approximately 70 μm and dried in a vacuum oven at 120 °C overnight to remove moisture and residual ethanol. Circular-shape electrodes of 14 mm in diameter were punched out from the dried film before pressed onto aluminum foil current collectors. Subsequently, 2025 stainless-steel coin cells with two carbon electrodes with similar mass separated by a piece of microporous separator (Celgard 3501) were assembled inside an argon-filled glove box (both of oxygen and H₂O contents were less than 0.1 ppm). Commercial 1 M tetraethylammonium tetrafluoroborate (TEABF₄) in acetonitrile (AN) was used as electrolyte. The mass loading of active material on each electrode was about 5–6 mg.

The electrochemical performance of the PCNCs based electrodes were evaluated by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS). The potential ranges of CV were of 0–2.7 V with scan rates of 10–300 mV/s. The current density for the GCD measurements varied from 1 to 30 A/g based on the mass of a single electrode within the voltage range of 0–2.7 V. EIS was measured were recorded in the frequent ranges from 10^5 Hz to 10^{-2} Hz at the open circuit voltage with an AC amplitude of 5 mV. The cycle-life stability was tested using LAND CT2001A testing instrument (Wuhan Land Co., China) at a current density of 5 A/g for 5000 cycles within 0–2.7 V. The gravimetric specific capacitances were calculated on the basis of the discharge curve according to the equation $C_s = 2(I\Delta t/\Delta V)$, where I (A/g), Δt (s), and ΔV (V) are the current densities, the discharge time, and the discharging potential window (2.7 V), respectively. The energy density (E , Wh/kg) and the power density (P , W/kg) of the supercapacitors were determined according to $E = C_s\Delta V^2/8$ and $P = E/\Delta t$, respectively.

3. Results and discussion

Fig. 1 shows a schematic illustration of the preparation process for PCNCs via the following steps: a) direct carbonation of sodium polyacrylate under inert atmosphere leading to formation of CNCs; b) subsequent chemical activation with KOH was employed to generate

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