Research Paper

Fast charge rate supercapacitors based on nitrogen-doped aligned carbon nanosheet networks

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A B S T R A C T

Achieving high electrochemical energy density while retaining high power density still remains a great challenge for porous carbons as the electrodes for supercapacitors. We report a facile and scalable synthesis of N-doped aligned carbon nanosheet network (N-ACN10) with high surface area and efficient 3D ion and electron transport pathways. Moreover, 3D interconnected nanochannels parallel to the graphene planes are beneficial for the increased ion accessible surface area and fast ion diffusion. Benefiting from fast ion and electron transport kinetics, the N-ACN10 electrode exhibits excellent frequency response with a scan rate up to $5\,V\,s^{-1}$, high capacitance of $331\,F\,g^{-1}$ at $2\,mV\,s^{-1}$ and superior rate capability ($203\,F\,g^{-1}$ at $5\,V\,s^{-1}$), as well as excellent cycling stability (98% of capacitance retention after 10,000 cycles) in 6 M KOH. More importantly, the assembled N-ACN10//N-ACN10 supercapacitors exhibit outstanding electrochemical performances in $1\,M$ Na_2SO_4 and $EMIMBF_4$ electrolytes with maximum energy densities of 20.6 and $120.4\,Wh\,kg^{-1}$ based on the mass of total active material, respectively.

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1. Introduction

Nowadays, the rapidly growing demand for green and sustainable energy has attracted numerous research efforts on the design and development of advanced energy storage devices [1,2]. Supercapacitors based on porous carbon can deliver high power density with long cycle life through the electrical double-layer capacitance (EDLC) formed at an electrode-electrolyte interface. However, their energy densities are much lower than those of batteries, and their charge and discharge rates are often less than $1\,V\,s^{-1}$ [3]. Recently, the design of microconfiguration (micro-supercapacitors) or the use of ultra-thin active material on the current collectors can provide high power densities with an fast-charge/charging rate above $10\,V\,s^{-1}$ due to short ion transport length, but their specific capacitances and energy densities based on weight or areal are much lower compared to conventional supercapacitors [4,5]. Furthermore, pseudocapacitor *via* charge transfer during surface chemical reactions can provide more energy than electrical double-layer capacitor (EDLC), but this situation is only realized at low charge rates due to their poor rate

performance and severe self-discharge [6–8]. Therefore, exploring new electrode materials for further improvement of the energy of supercapacitors especially at fast rates exceeding $1\,V\,s^{-1}$ is very urgent.

The specific capacitance and energy storage characteristics of EDLC are strongly depended on the surface area of porous carbons determined by microporous structure [9], however, large pore tortuosity and poor pore connectivity of micropores severely slow down the ion transport to the surface of carbon, thus limiting the power characteristics [10,11]. By contrast, mesoporous carbons with high electrical conductivity often have high power density of EDLC due to their fast ion/electron transport within the electrode particles. Soft and hard templating methods are commonly employed for the preparation of mesoporous carbons with controlled pore sizes and tunable pore connection [12–14]. However, the complicated and expensive multilayer synthesis process limits their practical applications. Graphene materials with good electrical conductivity, mechanical strength, and specific surface area, are expected as promising candidates for satisfying high energy and power density requirements for supercapacitors [15,16]. Unfortunately, the agglomeration or restacking of graphene sheets during the preparation and charge and discharge process, leads to the decreased surface area and ion diffusion with cycling, resulting in moderate electrochemical

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performances [17]. Therefore, in order to obtain superior rate capability for energy storage devices, the design of carbon-based materials with high ion accessible surface areas and short diffusion distance ensuring rapid mass and charge transport is highly desirable [18–20].

Here, we present a novel strategy for the design of N-doped aligned carbon nanosheet network (N-ACN10) through the carbonization and N-doping process of potassium citrate using MgO nanosheets as template (Scheme 1). Due to its high surface area, high conductivity and efficient 3D ion transport pathways, the as-obtained N-ACN10 shows a high specific capacitance of 331 F g^{-1} at 2 mV s^{-1} with superior rate capability (203 F g^{-1} at 5 V s^{-1}), and excellent cycling stability in 6 M KOH. Furthermore, the as-assembled supercapacitor delivers high energy densities of 20.6 Wh kg^{-1} in 1 M Na$_2$SO$_4$ and 120.4 Wh kg^{-1} in EMIMBF$_4$.

2. Experimental Section

2.1. Synthesis of N-ACN10, and CS

The synthesis of MgO nanosheets template was described by our previous work [21]. Briefly, 50 mg MgO nanosheets template was mixed with 500 mg potassium citrate (Tianjin Hengxing Chemical Reagent Co., Ltd., China) through a facile grinding approach. After that, the mixture was sealed in a quartz tube furnace then heated at 850 °C for 1 h with a heating rate of 3 °C min^{-1} in the mixture of N$_2$/NH$_3$ (N$_2$: 0.04 L min^{-1}, NH$_3$: 0.02 L min^{-1}) atmosphere. After that, the powder was purified by using 25 wt% HCl for 24 h to remove template, and followed by filtration and drying. The as-obtained carbon was named as N-ACN10. For comparison, interconnected carbon sheets (CS) were synthesized without MgO template. N-ACNx samples were synthesized by using the above mentioned process, where x refers to the mass ratios of potassium citrate to MgO (x = 5, 20). Reduced graphene oxide (RGO) was synthesized according to previously reported work [22], and commercial activated carbon YP-50 (BET surface area of 1417 m^2 g^{-1}) was purchased from Kuraray Chemical, Co., Japan.

2.2. Material Characterizations

Field-emission scanning electron microscope (SEM, Camscan Mx2600FE) and transmission electron microscope (TEM, JEOL JEM2010) were used to investigate the microstructural characterization. The specific surface areas and pore distribution were characterized by N$_2$ adsorption at 77 K with a NOVA 2000 (Quantachrome, USA) and calculated based on the Brunauer-Emmet-Teller (BET) method and the functional theory (DFT) model. TGA curves were performed on a thermal analyzer (STA 449 F3) from room temperature to 800 °C (10 °C min^{-1}) under N$_2$ atmosphere. The crystal structures were characterized by X-ray diffraction (XRD) equipped with Cu Kα radiation (λ = 0.15406 nm)
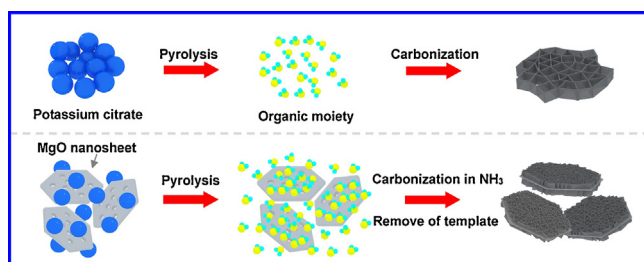
and Raman spectra were obtained by Jobin-Yvon HR800 Raman spectro-meter. X-ray photoelectron spectroscopy (XPS) was performed by PHI5700ESCA spectrometer with a monochromated Al Kα radiation (hv = 1486.6 eV) and the data acquisition were based on XPSPEAK software.

2.3. Electrochemical Measurements

The working electrodes were prepared by coating the mixture slurry onto nickel foam (1 cm × 1 cm). Briefly, active material, carbon black and poly binder (polytetrafluoroethylene) were mixed together in the mass ratio of 75:20:5 with a few drops of ethanol. After that, the as-prepared electrodes were dried at 100 °C for 12 h. The mass loading of the electrode material was about 2 mg. The three-electrode electrochemical tests were using 6 M KOH aqueous solution as the electrolyte. The as-prepared electrode, platinum foil and Hg/HgO electrode was used as the working electrode, counter and reference electrodes, respectively.

The symmetric supercapacitors were assembled by using two electrodes with same mass loading in 1 M Na$_2$SO$_4$ electrolyte and the voltage range is 0-1.6 V. The symmetric two-electrode cell using EMIMBF$_4$ as ionic liquid electrolyte was assembled in a glove box. A porous separator was placed between the two electrodes in a geometrical coin cell (CR2032 size). All the electrochemical tests were measured at a Solartron analytical 1400 electrochemical workstation.

For the symmetric supercapacitors, specific capacitance (C_s) was calculated by the formula (1). And for the symmetric cell, total cell capacitance (C_{cell}) was calculated by the formula (2). The energy density (E) and power density (P) were calculated according to the formula (3) and (4), respectively.

$$C_s = \frac{\int I dV}{m v \Delta V} \tag{1}$$

$$C_{cell} = \frac{I}{m(dV/dt)} \tag{2}$$

$$E = \frac{1}{2} C \Delta V^2 \tag{3}$$

$$P = \frac{E}{\Delta t} \tag{4}$$

For all above the formula, I is current density, m is the mass of the electroactive material of both working electrode, v is scan rate and ΔV is potential window, and Δt is the discharge time.

The frequency-dependent capacitance $C(w)$, the real part of accessible $C'(w)$ capacitance and the imaginary part $C''(w)$ were calculated according to the formula (5), (6) and (7), respectively.

$$C(w) = C'(w) - jC''(w) \tag{5}$$

$$C'(w) = \frac{-Z''(w)}{w|Z(w)|^2} \tag{6}$$

$$C''(w) = \frac{Z'(w)}{w|Z(w)|^2} \tag{7}$$

where $Z(w)$, $Z'(w)$ and $Z''(w)$ corresponding to the complex impedance, real parts and imaginary parts, respectively. Besides, w is defined as a function of frequency $w = 2\pi f$. To evaluate the

Scheme 1. Schematic representation of the formation of N-doped aligned carbon nanosheet network.