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High-frequency supercapacitors based on doped carbon nanostructures

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ABSTRACT

Carbon nanostructures are promising materials for electrochemical energy storage but their frequency response is usually poor, limiting their utilization in high-frequency applications. Here we demonstrate the growth of carbon nanostructures with different dopants of N, B, P/N, B/N, and Si, based on a scalable aerosol-assisted chemical vapor deposition process. The doped carbon nanostructures were directly grown on the conductive Ni substrates and exhibit an open and porous structure which is beneficial for fast ion transport and ion kinetics. Coin cells made of the doped carbon nanostructures demonstrate a frequency response as fast as 13,200 Hz at a phase angle of $-45°$ and the smallest relaxation time constant of ~77 μs. Together with a low equivalent series resistance and a large areal capacitance, the high-frequency supercapacitors based on doped carbon nanostructures could be promising in replacing traditional aluminium electrolytic capacitors for many high-frequency electronic devices.

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1. Introduction

Supercapacitors are advanced energy storage devices with outstanding attributes of low weight, high power density, long lifespan and safe operation [1–3]. They play a crucial role in the development of portable electronics, hybrid electrical vehicles, implantable biomedical devices, renewable energy applications [4–6], and more recently, in alternating current (AC) line filtering technologies [7,8]. AC line filters are used to attenuate the leftover AC ripples on direct current (DC) voltage busses, which provide buffers to filter out high-order harmonics and protect against electrical power surges and spikes [9–11]. They are particularly important for the efficient exploitation of renewable electrical power generated by photovoltaics or wind turbines, in which frequency variance can be caused by uncontrollable sunshine or wind flow [12]. To date, aluminium electrolytic capacitors (AECs) are widely employed in AC line filters. However, because of their low specific capacitance, AECs usually occupy the largest space and volume in the electronic circuits [13]. Replacing AECs with more compact, higher specific capacitance supercapacitors (usually 2–5 orders of magnitude higher than that of AECs) will thus have an immense impact on miniaturizing future electronic devices.

Unfortunately, the frequency response of most supercapacitors is slow in spite of their high power density. The commercial supercapacitors based on activated carbons behave comparable to a resistor rather than a capacitor at the frequency of ~1 Hz, far below the required operating frequency of 120 Hz in AC line filtering. The poor frequency response of commercial supercapacitors arises from a number of factors, such as impeded ion accessibility, long ion diffusion length, slow charge transfer rate (*e.g.*, Faradaic redox reactions), and low electrical conductivity [14,15]. In addition, the torturous pore structure observed in most supercapacitor electrodes, which is beneficial for obtaining a large surface area, can limit ion transportation and thus ion kinetics [16]. An effective strategy to overcome these limitations and improve the frequency response is by designing the electrode materials with an open structure and minimized tortuosity [12,15]. Both ordered mesoporosity and vertical alignment have been demonstrated on novel carbon nanostructures, such as carbon nanotubes (CNTs), graphene,

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and porous carbon, to improve the frequency response [8,9,15,17]. For example, the seminal work by Miller et al. reported a super-capacitor based on vertical graphene electrodes which could be charged and discharged within millisecond while maintaining the capacitive behavior [9]. Yoon et al. also demonstrated reduced graphene oxide (VArGO) film by cutting graphene oxide rolls with rotary cryomicrotome and observed very fast electrolyte ion diffusion [17]. Nevertheless, the fabrication of these electrodes often involved complicated and high-cost steps. The specific capacitance of these fast-response supercapacitors, particularly at the frequency of 120 Hz, also remains to be improved to fulfill the requirements in practical devices.

Here, based on an aerosol-assisted chemical vapor deposition (AACVD) process, we demonstrate that N−, B−, P/N-, B/N- and Si-doped carbon nanostructures can be directly grown on conductive Ni substrates. We show that binder-free electrodes could be fabricated in a single and scalable process. The doped carbon electrodes exhibit a capacitive behavior at the frequency of 120 Hz and a fast kinetic response with the characteristic frequency up to 13,200 Hz, 3 to 4 orders of magnitude higher than that of commercial supercapacitor electrodes. Furthermore, symmetric coin cells assembled from the doped carbon nanostructures indicate a low electrical resistance and a large areal capacitance arising from the enhanced charge storage at the dopant/defect sites. These results thus show a promising candidate for replacing AECs in AC line filters, shedding light on the design of suitable microstructures for high rate, fast response electrochemical energy storage devices.

2. Experimental

2.1. Growth of doped carbon nanostructures

We synthesized carbon nanostructures with various dopants in an AACVD process, originally developed for the growth of CNT arrays on the insulating quartz substrates [18,19]. Briefly, the pristine carbon nanostructure was obtained with the precursor solution of 5 wt% purified ferrocene ($Fe(C_5H_5)_2$) in ethylbenzene ($C_6H_5CH_2CH_3$). Ni foil was cut into discs with a diameter of 12 mm, then loaded on a Si wafer holder and inserted into a quartz tube (see Fig. S1). A piezo-driven aerosol generator was connected to the quartz tube placed in a 50 cm long horizontal electrical furnace. The quartz tube was then annealed to 800 °C under Ar atmosphere. When the growth temperature of 800 °C was reached, the precursor was carried into the quartz tube by Ar gas at 1 standard litre per minute (slm) and the growth was maintained for 15 min.

AACVD procedures similar to those used for pristine carbon structures were performed for producing N−, B−, P/B-, B/N- and Si-doped carbon electrodes. To optimise deposition rates of the different electrode materials, a combination of different precursors, synthesis temperatures and time were applied: (i) N-doped carbon were obtained using the precursor solution of 5 wt% purified ferrocene in benzylamine ($C_6H_5CH_2NH_2$), with a prolonged growth time of 60 min at 800 °C due to a slower growth rate compared to the standard carbon samples. (ii) 7.5 wt% purified ferrocene in ethylbenzene mixed with 2.5 v% triethylborane (($C_2H_5)_3B$) in 1 M hexane were used to generate B-doped carbon at 900 °C for 30 min [20]. (iii) P/N-doped carbon was synthesized using 7.5 wt% purified ferrocene and 2.5 wt% triphenylphosphine (($C_6H_5)_3P$) in benzylamine at 900 °C and the synthesis time was set to 60 min. Here, P/N-doped instead of P-doped carbon was synthesized as it was previously shown that in the growth of CNT arrays phosphorus alone inhibited nanotube growth due to catalyst poisoning [21,22]. (iv) For B/N-doped carbon a precursor consisting of 7.5 wt% purified ferrocene in a mixture in the ratio 1:1 of benzylamine and ethylbenzene mixed with 2.5 v% triethylborane in 1 M hexane was used.

The synthesis was conducted at 900 °C for 60 min (v) 2.5 wt% triphenylsilane (($C_6H_5)_3SiH$) in ethylbenzene in conjunction with 7.5 wt% purified ferrocene was used for the Si-doped carbon materials. The samples were obtained after 30 min growth at a temperature of 900 °C.

2.2. Materials characterization

The morphology of doped carbon nanostructures was characterized by scanning electron microscopy (SEM; JEOL 6500F) at an accelerating voltage of 5 kV and a working distance of 6 mm. Transmission electron microscopy (TEM; JEOL 3000F) was at an accelerating voltage of 300 kV. Samples for TEM were prepared by dispersing doped carbons in ethanol with ultrasonication, dropping on holey-carbon coated copper grids, and drying in air. Raman spectroscopy (Horiba Jobin-Yvon LabRAM ARAMIS) used Ar laser excitation at 532 nm. X-ray photoelectron spectroscopy (XPS; Thermo Scientific K-alpha 128-channel detecting analyzer) used an Al Ka source at 1486.6 eV. XPS peak analyses were performed using XPSPeak 4.1.

2.3. Coin cell supercapacitor assembly

To simulate practical device behavior, symmetric electrochemical coin cells of type CR2032 were fabricated using carbon nanostructures without any binders or conductive additives [23,24]. In brief, two identical carbon electrodes were placed on stainless steel (type 304; Zapp Precision Metals) current collectors as binder-free electrodes. Polyethylene was used as the separator and 1 M tetraethylammonium tetrafluoroborate (TEABF$_4$) in acetonitrile (AN) was used as the electrolyte owing to its high ion conductivity and better ion penetration inside the porous structure of the carbon-based materials [25]. The devices were assembled in an argon-filled glovebox system with an area of active materials of 1.13 cm^2 per electrode.

2.4. Electrochemical measurement

The electrochemical measurements of coin cells were conducted on a potentiostat (BioLogic VMP3). Cyclic voltametric (CV) curves were obtained at a potential window of 2.5 V with scan rates varying from 5 to 500 mV s^{-1}, while galvanostatic charge/discharge (CD) curves were obtained at constant current densities of 0.044—0.88 mA/cm^2. Electrochemical impedance spectra (EIS) were conducted by applying 10 mV sinusoidal signal at open circuit potential in the frequency range of 100 kHz to 10 mHz. Areal capacitance C_a of carbon nanostructures was calculated based on the discharge curves of galvanostatic CD measurements by $C_a = 2I \times \Delta t/V$, where I is the current density, Δt is discharging time, and V is the potential window (i.e., 2.5 V). C_a at the frequency of 120 Hz is calculated based on the EIS spectra using $C_a = -2/(2\pi f \times Z'')$, where f is the frequency of 120 Hz and Z'' is the imaginary part of the complex impedance Z. The calculated C_a is equivalent to single electrode capacitance obtained in a three-electrode configuration. It is noteworthy that C_a is used instead of the gravimetric specific capacitance C_s in order to more precisely describe the practical devices and to avoid inaccurate measurement of low density material on the electrodes [23,26].

2.5. Frequency response analysis

One of the simplest ways to describe the supercapacitor frequency behavior is to associate a serial resistance R and an ideal capacitance C [25]. The impedance of a resistor and a capacitor in series is given by,