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Communication

Boron and nitrogen dual-doped carbon as a novel cathode for high performance hybrid ion capacitors

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ABSTRACT

Hybrid ion capacitors have been considered as a very attractive energy source with high energy density and power density since it combines both merits of lithium ion batteries and supercapacitors. However, their commercial application has been limited by the mismatch of charge-storage capacity and electrode kinetics between the capacitor-type cathode and battery-type anode. Herein, B and N dual-doped 3D superstructure carbon cathode is prepared through a facile template method. It delivers a high specific capacity, excellent rate capability and good cycling stability due to the B, N dual-doping, which has a profound effect in control the porosity, functional groups, and electronic conductivity for the carbon cathode. The hybrid ion capacitors using B, N dual-doping carbon cathode and prelithiated graphite anode show a high energy density of 115.5 Wh/kg at 250 W/kg and remain about 53.6 Wh/kg even at a high power density of 10 kW/kg. Additionally, the novel hybrid device achieves 76.3% capacity retention after 2000 cycles tested at 1250 W/kg power density. Significantly, the simultaneous manipulation of heteroatoms in carbon materials provides new opportunities to boost the energy and power density for hybrid ion capacitors.

With the rapid development of portable electronics and hybrid electric vehicles, there has been an urgent need for advanced energy devices with both high energy and power density as well as a long cycle life. Among various energy storage systems (ESS), lithium ion batteries (LIBs) and supercapacitors (SCs) are considered to be very attractive energy devices and dominated the markets in our daily life [1–4]. LIBs can deliver high energy density by the faradic redox mechanism, however, the power densities are limited and cycling life is poor [5–7]. Although SCs can offer high power densities and long cycling life, a relative unsatisfactory energy density due to the physical adsorption/desorption mechanism has restricted their wide application in the automotive industry [8–10]. Therefore, designing a novel ESS which can simultaneously combined the advantages of both LIBs and SCs has become an important research direction in the field of energy storage.

Hybrid ion capacitors (HIC), a kind of asymmetric supercapacitor with a battery-supercapacitor hybrid energy storage mechanism, bridges the gap between LIBs and SCs and has attracted tremendous research interest in recent years [11–14]. Generally, the lithium ion capacitors (LICs) composed of a high capacity battery-type anode and a high rate capability capacitor-type cathode in organic electrolytes containing Li salts. In the typical LICs, high surface area commercial activated carbon, Li^+ intercalation compounds such as graphite [15,16], $Li_4Ti_5O_{12}$ [17,18], TiO_2 [19], Nb_2O_5 [20], Li_3VO_4 [21], hard carbon [22], soft carbon [23] and graphene [24,25], are usually used as the cathode and anode materials, respectively. Owing to the Li^+ redox reaction is much slower than the anion adsorption/desorption process, thus the power performance was determined by the anode materials. Numerous researches have paid attention to improve the rate capability of various anode materials [26–28]. Actually, the energy characteristic of LICs depends on the cathode, although the commercial activated carbon (AC) having a high surface area up to 3000 m^2/g, unfortunately, the specific capacitance of AC is limited by its inherent defect. Thus, designing a novel carbon material with excellent comprehensive performance used for the LICs is very meaningful.

Recently, modifying the physical and chemical properties of carbon-based materials to improve energy storage performance by

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doped the heteroatoms has attracted attention. It is found that the nitrogen (N) atoms doping can not only enhance the capacity of active materials through pseudocapacitance contribution but also promote electronic conductivity through doping effect [29]. Furthermore, the wettability and contact of carbon surface with electrolyte could be improved by the N atoms doping [30,31]. Besides that, the boron (B) atom is an electron-deficient alternative to N atoms, which has a similar function and effect [32,33]. Nevertheless, to the best of our knowledge, still little attention has been paid to the B and N dual-doped carbon materials as cathode for LICs.

In this work, we used nano-$CaCO_3$ as template and sucrose as carbon source to synthesis honeycomb-like structure carbon cathode. The N and B atoms could dope into the 3D structure carbon easily by *in situ* activate process with ammonium borate ($NH_4HB_4O_7{\cdot}3H_2O$) as an additive reagent. It was demonstrated that the B, N dual-doping has a significant effect in tuning the porosity, functional groups, electrical conductivity of the carbon cathode, and a higher specific capacity as well as excellent cycling performance has been achieved. Besides, the LICs have been assembled by using the B, N dual-doped carbon as the cathode and pre-lithiation graphite as the anode. Benefit from the synergistic effect of the B, N dual doping, the novel LICs shows 115.5 Wh/kg at 250 W/kg and remains at 53.6 Wh/kg even at a high power density of 10 kW/kg with a stable cycle life, which delivers a superior electrochemical performance than by using conventional carbon cathode material.

The morphologies of commercial nano-$CaCO_3$, CC and BNC were characterized by SEM as shown in Fig. 1 and Fig. S1 (Supporting information), respectively. The particle size of the nano-$CaCO_3$ was *ca.* 40–200 nm and a majority of them with about 40 nm (Figs. S1a and b in Supporting information). It should be noted here that the nano-$CaCO_3$ is very cheap template, which can be easily dispersed in carbon precursor and removed with diluted HCl instead of the corrosive HF acid [34]. In addition, the $CaCO_3$ template could be used as activator during the carbonization process, which provides a very simple and easy preparation for mass production [35]. Both of the CC and BNC cathodes show a honeycomb-like structure. The nano-$CaCO_3$ in the precursor matrix works as templates for the mesopores and macropores structure after the acid pickling process (Figs. 1a and b, Figs. S1c and d in Supporting information). In fact, there are a lots of micropores derived from the self-activation process of nano-$CaCO_3$, which can be demonstrated by TEM measurement. As shown in Fig. 1c, the BNC delivered a 3D cross-linked superstructure and the thin carbon nanosheets were uniform distribution. Moreover, the high-resolution TEM (HRTEM) (Fig. 1d) revealed that the BNC nanosheets consist of well-developed amorphous structure with partial graphitic layer (insert the red arrow). The hierarchical porous carbon materials are beneficial to ion rapid transmission and the B, N dual-doped can significantly increase the active sites, improving the electrode kinetics of the carbon cathode.

To further study the microstructure of the CC and BNC cathode, the XRD patterns were performed in Fig. 2a. Two broad peaks at around 24° and 43° can be observed from all the carbon cathodes, corresponding to the crystallographic planes of (002) and (100) in the disorder carbon structure, which were consistent with the HRTEM results. It needs to be emphasized that the diffraction peaks of BNC slightly shifted to larger angles, exhibiting relatively high levels of graphitic character [36]. In addition, Raman spectra of the CC, BNC-0.5, BNC and BNC-2 are shown in Fig. 2b and Fig. S2 (Supporting information), the D band at 1350 cm^{-1} is assigned to defective or disordered graphitic structures, while the G band at 1580 cm^{-1} corresponding to the orderly graphitic layers structures. The I_D/I_G ratio of BNC-0.5, BNC and BNC-2 are smaller than that of the CC, suggesting that the degree of graphitization has been enhanced, which can be also proved by the XRD results.

The XPS analysis was performed to confirm the incorporation of heteroatoms in the 3D honeycomb-like carbon material. The survey XPS spectrum demonstrated the presence of C 1s, O 1s, B 1s and N 1s without any other impurities (Fig. S3 in Supporting information), indicating the successful B and N atoms doping by this simple method. The XPS revealed that the atomic percentage of B and N in BNC was 4.43% and 6.99%, respectively. In addition, the doping amount could be changed by adjusting the concentration of $NH_4HB_4O_7{\cdot}3H_2O$ (Table S1 in Supporting information). The high-resolution of B 1s spectrum could be divided into two components at 190.8 and 191.9 eV (Fig. 2c), corresponding to B-N/BC_3 and B-C_2O/B-CO_2 bonds, respectively [37]. Additionally, the

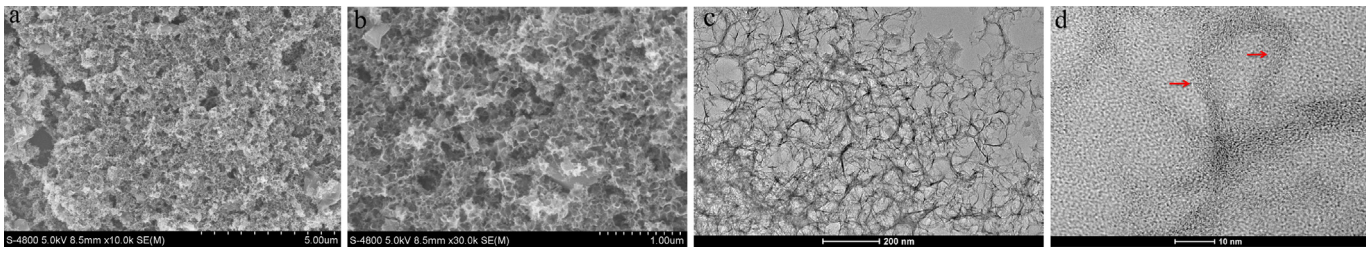

Fig. 1. SEM (a, b) and TEM images (c, d) of BNC cathode.

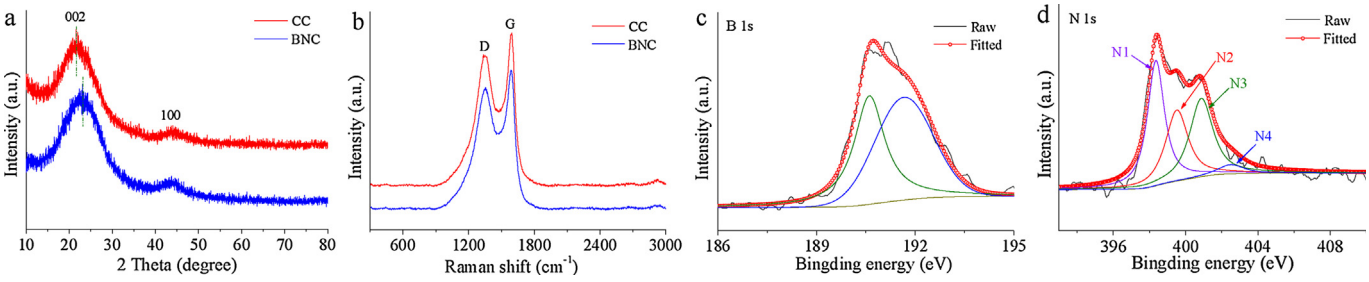

Fig. 2. (a) XRD patterns and (b) Raman spectra of the CC and BNC. High-resolution B 1s (c) and N 1s (d) XPS spectra of the BNC.

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