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# High-performance symmetric supercapacitors based on carbon nanosheets framework with graphene hydrogel architecture derived from cellulose acetate

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## HIGHLIGHTS

- N-doping carbon nanosheets framework (N-CNF) is fabricated from cellulose acetate.
- The N-CNF shows an architecture like hydrogel with high specific surface area.
- The N-CNF exhibits excellent rate capability and high specific capacitance.
- A single symmetric supercapacitor easily lights 60 red light-emitting diodes.

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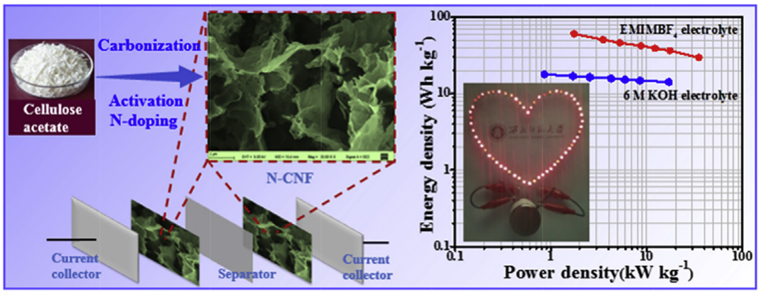
## GRAPHICAL ABSTRACT



## ABSTRACT

Three-dimensional nitrogen-doped carbon nanosheets framework (N-CNF) has been obtained starting with cellulose acetate. The product is prepared through a so-called one-step method that carbonization, activation and nitrogen-doping occur simultaneously. The resultant N-CNF shows an architecture like graphene hydrogel with interconnected hierarchical porous structure, N-doping with high nitrogen content (8.7 wt%) and high specific surface area (1003.6 m$^2$ g$^{-1}$). The N-CNF electrode displays excellent electrochemical performances due to the unique architecture and pseudocapacitance contribution from heteroatoms. In the three-electrode configuration, the N-GNF achieves a high specific capacitance of 242 F g$^{-1}$ at 1 A g$^{-1}$ and displays ultrahigh rate capability (83.4% capacitance retention at 100 A g$^{-1}$) in 6 mol L$^{-1}$ KOH electrolyte. The symmetric supercapacitor (SSC) based N-CNF exhibits energy density as high as 60.4 Wh kg$^{-1}$ (at a power density of 1750 W kg$^{-1}$) and 17.9 Wh kg$^{-1}$ (at 850 W kg$^{-1}$) in ionic liquid and aqueous electrolytes, respectively. It is surprised that the single device filled by ionic liquid electrolyte is able to light easily 60 red light-emitting diodes (LEDs, 2.2 V) in parallel after charging for only 10 s, showing an excellent energy storage/release performance.

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## 1. Introduction

Carbon-based materials such as activated carbon (AC), carbon onion, carbon microsphere, graphene hydrogel, metal-organic framework (MOF) derived porous carbon and a series of biomass/natural organic polymer carbide-derived carbons (CDCs) have been the most widely used as electrode materials for supercapacitors [1–4]. As well-known, the capacitance (*C*) is a function that depends on the specific surface area (*A*) of electrode materials, that is $C = \varepsilon_r \varepsilon_0 A/d$ where the surface is accessible to electrolyte ions which can contribute to charge storage. The accessible specific surface area results in sufficient electrode-electrolyte contact area to form electric double layers [5–7]. Essentially, the magnitude of capacitance is determined by the accessible surface area for the carbon-based materials while the releasing behavior of capacitance is relative to the pore structures of the materials. It is generally considered that: the macropores (>50 nm) can serve as ion-buffering reservoirs to provide short diffusion distance for electrolyte ions; the mesoporous (2–50 nm) is similar to “highway” which facilitates the fast transport of electrolyte ions to the interior of the bulk materials; the micropores (<2 nm) is primarily responsible for the ions accommodation [8–11]; the ultra-microporous (<0.70 nm) has been reported to be linked to an anomalous increase in specific capacitance through the desolvation of ions [12,13]. A large amount of small pores may contribute to a relatively high specific capacitance at low current density, but at high discharge rate, these pores could be inaccessible, and accordingly results in a relatively poor rate capability [14]. In the case of small nanopores, the mass transfer of ions shows a limited feature in kinetics that is related to inner-pore resistance for ions transport and the long diffusion distance from electrolyte to the depths of pores. Therefore, the optimal pore structure and pore size are required to improve the capacitive performance of the electrode materials [1,14–16]. Besides, heteroatoms (such as N, O, S, B, and P) doping, especially nitrogen doping, has also the effect on capacitive behaviors in both aqueous and organic electrolytes. The doped heteroatoms can provide a pair of electrons that effectively change electron-donor characteristic, which regulates hydrophilic property or wettability of materials, enhances their electrical conductivity, and even generates pseudo-capacitive contribution [17–20].

The graphene hydrogel has been reported many times in the literature due to its cross-linked, three-dimensional (3D) and porous network architecture [21–23]. The graphene hydrogel is fabricated by using graphite oxide as building blocks. It not only inherits the advantages of two-dimensional graphene nanosheets but also holds a unique three-dimensional porous framework with excellent electrical conductivity, where the porous structure of 3D framework can provide open channels for continuously unobstructed transportation of electrolyte ions [24,25]. Moreover, the inter-connected architecture effectively prevents the parallel restack and agglomeration between graphene sheets driven by the strong π-π interaction, resulting in that most of the graphene sheets are exposed to electrolyte [26,27]. However, conventional preparation of the graphene hydrogel involves in the synthesis of graphite oxide, which needs to consume a big dose of chemical oxidants and undergoes a cumbersome procedure. This will limit its industrial application actually [17,28]. Therefore, it is necessary to develop an environmentally friendly and low-cost approach to synthesize a carbon-based material with graphene hydrogel-like architecture, especially, by using biomass and/or natural organic polymer as precursor [21,28]. Recently, some interesting works have been done aiming to synthesize a new type of 3D carbonaceous framework with excellent electrochemical performances. For example, Qiu and his group prepared porous carbon nanosheets (PCNS) through an integrated procedure of intercalation, pyrolysis, and activation by using bio-sources derived carbon precursors (gelatin). The as-made PCNS exhibited a high specific capacitance of 246 F $g^{-1}$ and an improved rate capability (82% capacitance retention at 100 A $g^{-1}$) [29]. Cao et al. fabricated hierarchically porous nitrogen-doped carbon (HPNC) nanosheets (NS) *via* simultaneous graphitization and activation of biomass-derived natural silk. The as-prepared HPNC-NS achieved a high specific capacitance of 242 F $g^{-1}$ and excellent rate capability [30]. Alireza Kohandehghan and his co-workers fabricated unique interconnected partially graphitic carbon nanosheets (CNS) (10–30 nm in thickness) with significant volume fraction of mesoporosity (up to 58%), good electrical conductivity (211–226 S $m^{-1}$) and high specific surface area (up to 2287 $m^2$ $g^{-1}$). The CNS which was prepared from hemp bast fiber through a hydrothermal process and then carbonization and activation showed outstanding electrochemical energy storage performance in ionic liquid electrolyte [31]. Wu et al. prepared sponge-like carbonaceous gels by using watermelon as the carbon source, and then used $Fe_3O_4$ nanoparticles to decorate the resultant 3D carbonaceous framework to form magnetite carbon aerogels (MCAs). The MCAs showed a very light weight and obtained a high capacitance of 333.1 F $g^{-1}$ and an excellent cycling lifetime for supercapacitors [32].

Cellulose acetate is an environmentally friendly and sustainable material, which can be obtained from natural cellulose through a simple esterification reaction. The analysis shows that cellulose acetate has a three-dimensional, highly cross-linked and macroporous structure, which might be beneficial to being used as a carbon resource to form carbon-based material with graphene hydrogel-like architecture. Herein, we reported a one-step strategy to prepare the three-dimensional, nitrogen-doped and ultrathin (~10 nm) carbon nanosheets framework (N-CNF), in which the cellulose acetate is used as starting material, urea as nitrogen source and $CaCl_2$ as activating agent. The N-CNF shows a graphene hydrogel-like architecture. Its high specific surface area and effective heteroatoms doping lead to an enhanced specific capacitance and outstanding rate capability of the electrode in the three-electrode configuration. The symmetrical supercapacitor assembled by using the N-CNF exhibits excellent electrochemical energy storage performance. A device filled by ionic liquid electrolyte is able to easily light 60 red light-emitting diodes (LED, 2.2 V) compounding in parallel after charging for only 10 s, showing a feature of high energy and power densities.

## 2. Experimental

### 2.1. Materials

Cellulose acetate, acetone, calcium chloride and urea. All the experiments were carried out using deionized (DI) water and analytical reagent.

### 2.2. Synthesis of nitrogen-doped carbon nanosheets framework (N-CNF)

The typical preparation procedure of N-CNF is as following: 4 g of cellulose acetate without any further treatment was mixed with 4.5 g of calcium chloride and 3 g urea in 70 mL acetone solution as an initial step. The mixed solution was continuously stirred and evaporated at 70 °C until it became a viscous solution. Then the viscous solution was further heated in a conventional oven to form carbon precursor. Carbonization and activation were firstly followed by annealing carbon up to 500 °C for 1 h under a $N_2$ atmosphere in a tubular furnace with ramp rate of 5 °C $min^{-1}$, and then heat ultimate temperatures (650, 750 and 850 °C) for 2 h. The resulting dark solid was ground to powder, washed with 1 M HCl

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