



# Sustainable synthesis of phosphorus- and nitrogen-co-doped porous carbons with tunable surface properties for supercapacitors



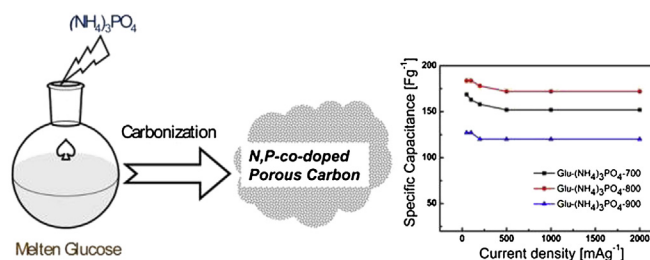
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## HIGHLIGHTS

- P, N co-doped porous carbons have been synthesized by a sustainable approach.
- P, N co-doped porous carbons exhibit tunable surface and textural properties.
- P, N co-doped porous carbons exhibit excellent supercapacitive performance.

## GRAPHICAL ABSTRACT



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## ABSTRACT

We report a simple yet efficient method to synthesize phosphorus- and nitrogen-co-doped glucose-derived microporous carbons with a simple inorganic salt (ammonium phosphate) as the single phosphorus and nitrogen source. The obtained products are typical microporous carbons with low surface area and narrow pore size distribution. The doping amount of oxygen, nitrogen, and phosphorus and the population of various functionalities were not only temperature-dependent, but also correlated with each other. The resultant samples exhibit a specific capacitance of  $183.8 \text{ F g}^{-1}$ , a capacitance retention ratio of over 90%, and an operating voltage up to 1.4 V in an alkaline electrolyte of 6 M KOH. The promising electrochemical performances can be attributed to the synergetic effect of (1) pseudocapacitance that originated from rich and tunable surface group by co-doping of phosphorus and nitrogen; and (2) the electric double layer capacitance that came from the uniform porosities developed by *in situ* activation.

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## 1. Introduction

Carbon materials are currently at the forefront of materials science due to their outstanding electronic, optical, mechanical, catalytic and electrochemical properties, especially in advanced energy conversion and storage fields [1–7]. As one of the most promising energy storage devices, electrochemical capacitor is of great interest due to its large specific energy, high power density,

and long durability for applications in hybrid electric vehicles, consumer electronics, or industrial power managements [4]. Despite specific capacitances are lower than that of conducting polymers or metal oxides, porous carbons triumph over their competitors in commercial devices because of their greater cycle stability and higher electrical conductivity [3–6]. Substitution of carbon atoms with heteroatoms (such as nitrogen [8], boron [9], phosphorus [10], and oxygen [11]) in the basal planes and/or at the edges endows them with exciting properties due to the tailored electronic structure and surface properties. Therefore, heteroatom-doped carbons have recently drawn much attention because of their potential applications in metal free heterogeneous catalysis,

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solar energy conversion, lithium ion batteries, and fuel cells [12,13]. Incorporation of foreign atom (oxygen [11,14], nitrogen [15], boron [16], sulfur [17], and/or phosphorus [18]) into porous carbon matrix has been proved a practical method to increase the energy density of supercapacitors due to the pseudocapacitance effects originated from Faraday reaction of surface functional groups [15,18,19].

Generally, heteroatom-doped porous carbons are prepared through carbonization of heteroatom-containing synthetic polymer precursors followed by an additional physicochemical activation [20–23] or replication from a hard template through nano-casting processes [24], which are tedious, time-consuming, costly, and harmful to environment. Another approach to prepare heteroatom-incorporated carbons is post treatment of a porous carbon, including surface oxidation, phosphoric acid activation [18,25], ammonia oxidation [26,27], or plasma treatment [28]. Recently, techniques and processes involved in the synthesis of heteroatom enriched porous carbon materials derive from sustainable precursors have attracted growing interest due to their low cost, energy and atom economy, and low toxicological impact of processes and materials themselves [29]. Oxygen-rich microporous carbons have been prepared through KOH activating of hydrochars derived from biomass (such as cellulose, starch, sawdust, and even fungi) by hydrothermal carbonization (HTC) [30] or one-step carbonization of a seaweed biopolymer [31,32]. Porous nitrogen-doped carbons have been produced by hydrothermal carbonization of chitosan or glucosamine followed by chemical activation [31,33].

The doping amount of heteroatom is dependent on the precursor, the surface chemistry, and the aromatization level of initial carbonaceous supports. Moreover, the development of surface functionalities is dependent on the temperature of heat treatment [34,35]. Understanding the role of heteroatom-containing groups on the electrochemical capacitive properties of carbon electrode is important for the application of the carbon-based supercapacitor. In fact, it is almost impossible to investigate the effect on the capacitive performance of mono heteroatom doping alone except for oxygen, because of the inevitable formation of oxygen-containing functionalities during the development of porosities. In addition, compared with mono heteroatom doping that improves merely one aspect of properties, co-doping (or tri-doping even multi-doping) can enhance overall performance of the materials due to the synergetic effect [36–38]. Therefore, more and more efforts have been focused on understanding the synergetic effects of multi-heteroatom doping in recent years. For nitrogen- and oxygen-co-doping which was extensively investigated, pseudocapacitive Faradic reactions were supposed to take place at the edges of graphene sheets on N-5, N-6 and O-I groups, while N-Q and N-X can help the transportation of electrons [14,18,38]. Recently, D. Hulicova-Jurcakova et al. have demonstrated that phosphorus- and oxygen-co-doping carbons exhibit an extraordinary electrochemical stability [18]. While the widening of the potential window has been accomplished by the blockage of the active oxidation sites with phosphorus groups. In spite of the existence of synergistic effects derived from different heteroatom-containing functionalities was commonly agreed, it is far from fully understood until now. The encountered problem lies in not only the complexity of the carbon surfaces but also the diversified development pathway of the heteroatom-containing surface groups [11,14,18,33,34,38–40]. Post-synthesis approach seems to be one practical way for the preparation of porous carbons with tunable surface properties, but this approach is costly, tedious and time-consuming [14,27,28,40,41].

Herein, we report a simple yet efficient method to synthesize phosphorus- and nitrogen-co-doped microporous carbons with tunable surface properties by using glucose as sustainable precursor and a simple inorganic salt (ammonium phosphate) as the

single nitrogen/phosphorus source. Different from post-animated treatment process, the heteroatoms (oxygen, nitrogen, and phosphorus) were doped homogeneously in the whole sample not just at the surface. The introduction of phosphorus into nitrogen- and oxygen-co-doped porous carbons has positive effects on overall capacitive performance and an improvement on the stability through the enhanced textural and surface properties.

## 2. Experimental

### 2.1. Materials preparation

In a typical example of synthesis, to a melting glucose (100 g), 80 g  $(\text{NH}_4)_3\text{PO}_4$  was added in small portions within 1 h, and the reaction proceeded for another 4–6 h at 180 °C until foaming ceased. The brown hygroscopic solid was stand still at 180 °C in a muffle furnace for several hours, then 350 °C over night. The resulting solid was carbonized under nitrogen at 700, 800, and 900 °C, respectively. The resulting monolithic foam was crushed into powder, and then washed thoroughly with hot water until neutral. The products were denoted as Glu- $(\text{NH}_4)_3\text{PO}_4$ -700, Glu- $(\text{NH}_4)_3\text{PO}_4$ -800, and Glu- $(\text{NH}_4)_3\text{PO}_4$ -900. For the sake of comparison, their phosphorus-free counterparts have been prepared from glucose with  $(\text{NH}_4)_3\text{PO}_4$  replaced by  $\text{NH}_4\text{Cl}$ , which were named Glu- $\text{NH}_4\text{Cl}$ -700, Glu- $\text{NH}_4\text{Cl}$ -800, and Glu- $\text{NH}_4\text{Cl}$ -900.

### 2.2. Characterization

X-ray diffraction (XRD, 40 kV, 100 mA) patterns were collected on a Rigaku D/Max2400 diffractometer equipped with a  $\text{CuK}\alpha$  radiation source. Nitrogen adsorption-desorption measurements were performed at 77 K with a Quantachrome Adsorption Instrument. Prior to the measurements, the samples were degassed at 150 °C for 4 h. The specific surface areas ( $S_{\text{BET}}$ ) were calculated with the Brunauer–Emmett–Teller (BET) equation in a relative pressure range from 0.06 to 0.35. The pore size distributions of the samples were obtained using the non-local density functional theory (NLDFT) approach. The elemental analysis was done by a conventional CHN combustion method (Vario EL-3) based on the burn-off of the sample with a thermoconductive detector (TCD). X-ray photoelectron spectroscopy (XPS, ESCALAB250, Thermo VG Corporation, USA) was used in the surface analyses of the samples.  $\text{AlK}\alpha$  line (15 kV, 10 mA, 150 W) was used as a radiation source, and the C1s peak position was set at 284.6 eV as an internal standard. The peak separations of the N1s and O1s core level peaks were estimated by least squares with Gaussian–Lorentzian functions after subtraction of background noise. The concentration of each element was calculated from the area of the corresponding peak calibrated with the atomic sensitivity factor using C as the reference. Scanning electron microscopy (SEM) investigations were carried out on a FEI Nova NanoSEM 450 equipped with an Oxford X-MAX energy dispersive X-ray spectroscope (EDS) for elemental analysis.

### 2.3. Electrochemical measurement

The capacitor electrodes with a diameter of 10 mm were obtained by pressing a mixture of the samples (80 wt%), carbon black (10 wt%) and polytetrafluoroethylene (PTFE) (10 wt%) onto the foam nickel collector. The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests were conducted using an electrochemical working station (CHI660D, Shanghai, China) in a three-electrode cell system, employing a platinum foil as the counter electrode, Hg/HgO as the reference electrode. CVs were recorded between –0.9 and –0.1 V at different scanning rates. The

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