



## Facile synthesis of nitrogen-doped porous carbon as robust electrode for supercapacitors



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### ABSTRACT

Porous carbon nanomaterials are highly attractive as electrode materials for supercapacitors (SCs), but the relatively low capacitance as a result of their intrinsic electric double-layer mechanism severely hinders their practical applications. In addition, the complicated preparation processes of most porous carbon nanomaterials previously reported is less impressive for large-scale application. In this work, we report an efficient and simple method to synthesize porous N doped carbon (PNC) on flexible carbon cloth as high-performance electrode for SCs. Benefiting from the unique porous architecture and high N dopant content, the as-fabricated PNC electrode delivers excellent capacitive performance. A high areal capacitance of  $682.8 \text{ mF cm}^{-2}$  at  $2 \text{ mA cm}^{-2}$  and outstanding cycling performance (less than 4% capacitance fading after 10,000 cycles) is achieved by this PNC electrode. This work opens up new opportunities in developing advanced carbon-based electrode for energy storage.

### 1. Introduction

Owing to the key advantages including outstanding power densities, rapid charge/discharge ability and ultralong life time, supercapacitors (SCs) have gained considerable interests from both scientific and technological researchers. [1–3] Extensive applications of SCs have been demonstrated in various fields, like electric vehicles, emergency power sources, renewable energy systems and many others. [4–6] To date, a wide range of materials have been explored as electrode materials for SCs, which can be mainly categorized into carbon materials, metal oxides and conducting polymers. [7–15] However, electrodes based on metal oxides and conducting polymers always suffer from poor rate capability and low cycling stability, which severely restricts their broad applications. [16–23] By contrast, relying on pure electronic double layer capacitance (EDLC), carbon materials with advantageous features of high conductivity and chemical/electrochemical stability have been considered as the mostly wide used commercial alternatives for SCs electrodes. [8,24–27] At present, the main challenge of carbon electrodes lies in their low specific capacitance, which further results in the low energy density of SCs based on these electrodes. [8,28–30] To fulfill the ever-growing energy demand of modern electronics, further boosting the specific capacitance of carbon

materials is of vital importance.

Since EDLC is dominantly controlled by the electrode structure and is strongly related to the accessible surface of electrodes, rationally designing porous structure is believed to be an effective approach to improve the specific capacitance of carbon materials. Particularly, carbon materials with multi-scale pores are preferred as favorable electrodes, as micro pores supply the main active sites, endowing high specific capacitance, while meso and macro pores offer efficient pathways for ionic transportation and diffusion, ensuring fast electrochemical response. [31,32] On the other hand, efforts have also been devoted to doping nitrogen into carbon materials with the motivation of introducing extra pseudo capacitance. [33–35] Numbers of previous studies have revealed the introduction of nitrogen is able to modify the electronic properties of carbon materials, further contribute to the improvement of specific capacitance. [36–41] For example, nitrogen-doped graphene was synthesized by decomposing cyanamide on graphene oxide nanosheets through thermal annealing of graphite oxide in  $\text{NH}_3$  atmosphere, showing a much improved specific capacitance of  $248.4 \text{ F g}^{-1}$  in comparison with that of non-doped graphene ( $51.7 \text{ F g}^{-1}$ ). [42] Yu et al. fabricated a kind of N-doped porous carbon nanofibers through carbonization of carbonaceous nanofibers coated with polypyrrole. [43] The as-obtained electrode exhibited an

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outstanding reversible specific capacitance of  $202.0 \text{ F g}^{-1}$  at the current density of  $1.0 \text{ A g}^{-1}$ . Mitlin et al. employed biomass-derived proteins (egg white) as precursor to prepare N-doped carbon material. [44] The as-obtained N-doped carbon through pyrolysis delivered a high capacitance of  $390 \text{ F g}^{-1}$  and an excellent cycling stability with 7% loss after 10,000 cycles. Despite these achievements, developing cost-efficient, easy-to-handle and scalable methods to fabricate porous N-doped carbon with high capacitive performance remains a huge challenge.

Herein, we demonstrate a facile and effective approach to fabricate porous N-doped carbon (PNC) material with superb capacitive performance. PNC was obtained through soaking carbon cloth into a mixture solution of inorganic salts as template, polyacrylonitrile (PAN) as carbon source, and dimethylformamide (DMF) as solvent, followed by pyrolysis and washing. Taking advantage of the unique porous structure and large amount of doped N, the as-obtained PNC electrode showed substantially enhanced capacitive behaviours when compared with the pristine C. In detail, the areal capacitance of PNC reached  $682.8 \text{ mF cm}^{-2}$  at  $2 \text{ mA cm}^{-2}$ , while the pristine C only exhibited a low areal capacitance of  $329.9 \text{ mF cm}^{-2}$ . All these results are hoped to provide more insights in the design of high-performance carbon materials.

## 2. Experimental section

### 2.1. Preparation of nitrogen doped porous carbon

All reagents used in this study were of analytical grade and were used without any additional purification. Nitrogen doped porous carbon (PNC) was obtained by soaking in precursor and annealing in a nitrogen atmosphere. Firstly, a certain amount of nickel (II) chloride hexahydrate ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ) was added into 15 mL DMF containing  $\text{ZnCl}_2$  (served as activator). After  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  dissolved completely at  $95^\circ\text{C}$ ,  $1.5 \text{ g 1-(2-pyridinylazo)-2-naphthaleno}$  (PAN) was added the solution and stirred about 20 min to obtain the precursor. Subsequently, Carbon cloth (C cloth) was soaked in the as-obtained precursor. After dried at  $60^\circ\text{C}$ , the C cloth with precursor was transferred into a tube furnace and further thermally annealed at  $800^\circ\text{C}$  in nitrogen atmosphere for 2 h. Finally, the as-prepared samples were washed with 3 M HCl solution to remove the metal, followed by washing with distilled water and ethanol and drying at  $60^\circ\text{C}$ . Non-porous N doped porous carbon (C) was also obtained via a similar route without adding  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  into the precursor. The mass loading of the PNC and C samples are about 3.7 and  $3.8 \text{ mg cm}^{-2}$ , respectively.

### 2.2. Materials characterization and electrochemical measurements

The morphology, structure, and composition of the electrode materials were characterized by field-emission SEM (FE-SEM, JSM-6330F), TEM (TEM, JEM2010-HR, 200 KV), and XPS (XPS, ESCALab250, Thermo VG). Nitrogen adsorption/desorption isotherms at 77 K were obtained on an ASAP 2020 V3.03 H instrument. All samples were out-gassed at  $100^\circ\text{C}$  for 5 h under flowing nitrogen before measurements. All the electrochemical measurements were conducted using an electrochemical work-station (CHI760). The electrochemical studies of individual electrodes were performed in a three-electrode cell, with a graphite rod counter-electrode and a saturated calomel electrode reference electrode, in 1 M KOH aqueous solution.

## 3. Results and discussion

Nitrogen doped porous carbon (PNC) was directly fabricated on carbon cloth by a simple and scalable approach (Fig. 1). The precursor gel made up of  $\text{NiCl}_2$  and PAN was first spread on the carbon cloth surface as carbon sources and nitrogen sources. Then, the carbon cloth coated with the precursor gel was annealed at  $800^\circ\text{C}$  in a nitrogen atmosphere and washed with acid and distilled water (details in

Experimental Section). Scanning electron microscopy (SEM) images in Fig. 2a and b reveal abundant Ni nanoparticles are uniformly embedded into carbon framework after calcination (denoted as Ni-NC). After acid etching, NPC with numerous pores was prepared (Fig. 2c). XRD patterns of the prepared Ni-NC and PNC samples are collected in Fig. 2d. Beside carbon peaks that come from the product and/or carbon cloth, Ni peaks are also observed for the Ni-NC, confirming the in-situ formation of Ni nanoparticles upon calcination. No any Ni peak was identified in PNC sample, showing these Ni nanoparticles have been completely removed after acid treatment. In addition, it should be pointed out that non-porous N doped carbon with smooth surface (denoted as C) was obtained when the precursor gel did not contain  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (Figs. S2 and S3). Transmission electron microscopy (TEM) analysis was further applied to study the detailed microstructure of products. As show in Fig. 2e, there were some pores in PNC samples compared to the pristine C (Fig. S4a), which was corresponding to SEM image. Moreover, the thickness of PNC was determined by the high-resolution transmission electron microscopy (HRTEM) image (Figs. 2f and S4b). However, no lattice fringe observed in PNC samples reveals that PNC samples are probably amorphous.

X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy measurements were carried out to investigate the surface state and composition of the products. Fig. 3a displays the XPS survey spectra of the pristine C and PNC samples. Both the samples only exhibit the presence of C, O and N elements, suggesting their high purity. In comparison to the pristine C sample, the N peak intensity of the PNC sample is much stronger, indicating the content of N is higher. The atomic N ratio was found to achieve 9.98% in PNC sample, while only 2.83% in pristine C sample. This indicates the presence of  $\text{NiCl}_2$  in the precursor can effectively enhance the content of N doping. [45] The increased N dopant in PNC sample is further confirmed by the core-level N 1s XPS spectra (Fig. 3b). The substantially higher N 1s peak intensity of the PNC sample clearly reveals its higher content of N. The peaks located at 398.0 and 400.2 eV correspond to the pyridinic and quaternary nitrogen, respectively. [42,46] Fig. 3c shows the core-level C 1s XPS spectra of the C and PNC samples, which can be deconvoluted into three peaks. The peak centred at 284.8 eV is attributed to the signals for graphite-like  $sp^2$  C, while the peaks at 285.9 and 287.1 eV are ascribed to the N- $sp^2$  C and N- $sp^3$ C, respectively. [46,47] The broader shoulder peak for the PNC sample suggests that it has more surface functional groups. Fig. 3d presents the Raman spectra of the samples. Two characteristic Raman peaks of carbon materials located at 1357 (D band) and  $1581 \text{ cm}^{-1}$  (G band) are observed for both the samples. Remarkably, the PNC sample shows a higher  $I_D/I_G$  ratio than the pristine C sample, reflecting its disordered carbon nature with abundant defects. [47] The Brunauer-Emmett-Teller (BET) surface area and pore volume for the PNC on carbon cloth are about  $25.5 \text{ m}^2 \text{ g}^{-1}$  and  $0.043 \text{ cm}^3 \text{ g}^{-1}$ , much higher than those of the pristine C on carbon cloth ( $9.4 \text{ m}^2 \text{ g}^{-1}$  and  $0.034 \text{ cm}^3 \text{ g}^{-1}$ ).

The electrical properties of pristine C and PNC electrodes were tested in a three-electrode cell with 1 M KOH as electrolyte. Fig. 4a compares the cyclic voltammogram (CV) curves collected for pristine C and PNC electrodes at a scan rate of  $100 \text{ mV s}^{-1}$ . Obviously, the PNC electrode exhibits a substantially higher capacitive current density than that of pristine C electrode, suggesting the substantially improved capacitance of PNC electrode. Fig. S4 shows the CV curves of the PNC electrode obtained at various scan rates. All of the CV profiles exhibit symmetric and nearly rectangular shapes, implying its superior charge storage ability and high efficiency. The corresponding areal capacitances were calculated and shown in Fig. 4d. Significantly, the PNC electrode achieved a remarkable areal capacitance of  $472.8 \text{ mF cm}^{-2}$ , which is higher than that of pristine C electrode ( $236.4 \text{ mF cm}^{-2}$ ). Additionally, a large capacitance of  $98.1 \text{ mF cm}^{-2}$  was still retained at the scan rate increased from 10 to  $200 \text{ mV s}^{-1}$ , indicating the good rate capability of PNC electrode.

The galvanostatic charging/discharging curves of the pristine C and

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