



# Nitrogen-doped hierarchically porous carbon foam: A free-standing electrode and mechanical support for high-performance supercapacitors

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## ABSTRACT

Free-standing 3D carbonaceous materials offer many advantages and therefore hold great potential for a wide range of applications. However, the synthesis of these materials often involves complicated processes that may lead to low yields and high costs. In this study, this issue is addressed through developing a facile, scalable, and cost-effective synthesis strategy. Nitrogen-doped hierarchically porous carbon foam (HP-CF) is fabricated by annealing of soft-template-casted melamine foam, and its application for supercapacitors is highlighted. The HP-CF integrates a large number of macropores and micropores, thus providing sufficient space for ion transport while offering a large amount of surface sites for energy storage, thanks to which the HP-CF exhibits a high capacitance of 238 F g<sup>-1</sup> (or 11.9 F cm<sup>-3</sup>). In addition, the HP-CF performs greatly when acting as the mechanical support for pseudocapacitive materials such as NiCo<sub>2</sub>S<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub>, based on which an asymmetric supercapacitor (ASC, can also be described as aqueous battery) is assembled. The ASC exhibits a high energy density of 93.9 Wh kg<sup>-1</sup> (or 3.55 mWh cm<sup>-3</sup>) and a high power density of 21.1 kW kg<sup>-1</sup> (or 799 mW cm<sup>-3</sup>), among the highest reported values for ASCs.

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## 1. Introduction

Free-standing 3-D carbon has attracted much research attention during recent years. In general, this type of materials is self-supported, mechanically flexible and compressible, electronically and thermally conductive, chemically stable, and rich in interconnected macropores. Benefiting from these advantages, 3-D carbonaceous materials have been explored for a variety of applications, such as electrochemical electrodes (e.g., supercapacitors [1], batteries [2,3], fuel cells [4], and solar cells [5]), absorbers [6], and matrixes for sensors [7] and thermal energy storage [8]. Currently, the synthesis methods of free-standing 3-D carbon can be mainly classified into four categories: self-assembly of graphene oxide (GO) (e.g., hydrothermal treatment [9,10], lyophilization [11,12], vacuum evaporation [13,14], and drop-casting [15]), chemical vapor deposition (CVD) [16], blowing of carbon precursors

[17], and carbonization of polymer foams [18–20]. Self-assembly of GO is a widely used method; however, 3-D reduced GO (rGO) often encounters problems such as  $\pi$ - $\pi$  restacking of rGO nanosheets and poor inter-sheet connections. Worse still, this method requires critical synthesis conditions and only produces 3-D rGO in small-scale. In order to synthesize high-quality graphene foam (GF), Cheng et al. proposed a CVD method by using Ni foams as the template [16]. This method demands careful manipulation of a complex growth process, making it difficult for commercialization. In addition, the CVD-grown graphene networks are relatively soft and can be torn easily.

To deal with the scalability problem of the previous two methods, Bando et al. synthesized 3-D strutted graphene in large quantities via pyrolysis of glucose assisted by a blowing agent [17]. Although 3-D carbon can be obtained, the morphology of the materials is irregular and hard to control due to the difficulty in structuring the precursor powders via pyrolysis. Also, the method requires a rather high processing temperature (1350 °C). Recently, it was demonstrated that 3-D carbon foams (CFs) can be fabricated by directly carbonizing commercially available polymer foams [18–20]. Despite the excellent mechanical characteristics of these CFs, their structures and properties are restricted by the raw-material –

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commercial melamine foams. An improved method to enable tuning of the material properties is highly desired.

In this study, we develop a facile, scalable, and cost-effective strategy to synthesize nitrogen-doped hierarchically porous carbon foam (designated as HP-CF) from the soft-template-casted melamine foam, and we demonstrate the application of the HP-CF in supercapacitors. Supercapacitors have been known for their excellent cycling stability and high power density, which promise diverse applications such as hybrid electric vehicles, cranes, forklifts, emergency back-up systems, etc. [21–24]. Since the capacitance of conventional supercapacitors, namely electric double-layer capacitors (EDLCs), depends on the surface area of the electrodes, enhancing the porosity (especially microporosity) of the electrode materials should be an effective route to enhance the supercapacitor performance. Hierarchically porous carbonaceous powders that integrate macropores and micropores have shown excellent performances for EDLCs, owing to the synergetic effect of macropores and micropores [25,26]. However, so far there have been few reports of free-standing 3D carbon materials with sufficient micropores.

Here, through templating the growth of melamine foams with structure-directing agent, we obtained HP-CF that contains not only the macropores that commonly exist in free-standing 3-D carbon materials but also a large amount of micropores. In addition, the HP-CF has a moderate density of approximately  $50 \text{ mg cm}^{-3}$ , which is 10-fold of that (approximately  $5 \text{ mg cm}^{-3}$  in average) of previously reported GFs and CFs [17,18,20,27,28]. Note that although the ultra-light-weight electrode materials can give a very high gravimetric capacitance, their volumetric capacitance is very low. For practical applications, volumetric energy density is as important if not more. Thanks to the hierarchically porous structure, the HP-CF is able to maintain a high volumetric capacitance of  $11.9 \text{ F cm}^{-3}$  while still delivering a high gravimetric capacitance of  $238 \text{ F g}^{-1}$ . In order to further improve the capacitance, we used the HP-CF as the mechanical scaffold to support the growth of pseudocapacitive materials,  $\text{NiCo}_2\text{S}_4$  and graphene/porous  $\text{Fe}_2\text{O}_3$  (denoted G- $\text{Fe}_2\text{O}_3$ ) [29], which can store and release considerably more charges than EDLC materials through redox reactions, and are used as the cathode and anode materials, respectively. The aqueous battery (called ASC in most reports) assembled from the above-mentioned electrode materials exhibits greatly improved energy and power densities, i.e.,  $93.9 \text{ wh kg}^{-1}/3.55 \text{ mWh cm}^{-3}$  at  $2.25 \text{ kw kg}^{-1}/84.9 \text{ mW cm}^{-3}$ .

## 2. Experimental section

### 2.1. Synthesis of nitrogen-doped hierarchically porous carbon foam (HP-CF)

All reagents were purchased from Aldrich unless otherwise specified. Typically, 3 g paraformaldehyde, 5 g melamine and 2 g Pluronic P123 (PEG-PPG-PEG) were added to a round-bottom flask containing 10 mL 0.5 M NaOH aqueous solution, followed by stirring and refluxing at  $85^\circ\text{C}$ . After 1 h reaction, the melamine resin was obtained, and was subsequently cooled down and mixed with 0.1 mL octylphenol polyoxyethylene ether (OP-10, purchased from HELM AG), 1 mL pentane and 0.3 mL formic acid under vigorous stirring. Then the as-obtained emulsion was solidified at  $80^\circ\text{C}$  for 4 h to form melamine foam. The carbonization of melamine foam was carried out in a tube furnace under an Ar atmosphere. The temperature was increased at a rate of  $1.5^\circ\text{C min}^{-1}$  from room temperature to  $350^\circ\text{C}$ ,  $5^\circ\text{C min}^{-1}$  from  $350^\circ\text{C}$  to  $800^\circ\text{C}$ , and then held at  $800^\circ\text{C}$  for 1 h. After washed in hot water and dried in an oven, the HP-CF was obtained. For comparison, a macroporous carbon foam with limited micropores was synthesized via a same

process except for adding P123, and was denoted Ma-CF. Similarly, a microporous carbon monolith (Mi-CM) with limited macropores was synthesized by a same process except for adding OP-10 and pentane.

### 2.2. Synthesis of $\text{NiCo}_2\text{S}_4$ in-situ grown onto the HP-CF

The melamine resin obtained in the above section was stirred and mixed with 0.1 mL OP-10, 1 mL pentane and 0.4 mL formic acid. Then this emulsion was further mixed with 2 mL aqueous solution of 2.4 mmol  $\text{Co}(\text{NO}_3)_2$  and 1.2 mmol  $\text{Ni}(\text{NO}_3)_2$  under vigorous stirring. Subsequently, the as-obtained emulsion was solidified at  $80^\circ\text{C}$  for 4 h to form a melamine foam, which was further annealed at  $800^\circ\text{C}$  for 1 h under an Ar atmosphere. After that, the product was immersed into a 0.1 M  $\text{Na}_2\text{S}$  aqueous solution that was contained in a Teflon-lined stainless steel autoclave, and then the autoclave was maintained at  $180^\circ\text{C}$  for 24 h. After cooling to room temperature, the product was washed with deionized water and ethanol several times, and dried at  $80^\circ\text{C}$ . The final product is designated as HP-CF@ $\text{NiCo}_2\text{S}_4$ .

### 2.3. Characterization

The morphologies and elemental compositions were characterized by a field emission scanning electron microscope (FE-SEM, Quanta F400) equipped with an energy dispersive X-ray spectroscopy (EDX) detector. A FEI Tecnai F20 transmission electron microscope (TEM) equipped with an EDX detector and a HAADF detector was used to further investigate the samples and take EDX maps. Olympus BHM microscope was used to capture optical microscope images. The compression/release test was conducted by an Instron 4486 mechanical tester equipped with two flat-surface compression stages and a 100 N load cell. The X-ray diffraction (XRD) patterns were collected using a Rigaku (RU300) diffractometer with  $\text{Cu K}\alpha$  radiation source ( $\lambda=0.1540598 \text{ nm}$ ). Investigations of chemical compositions were performed using X-ray photoelectron spectroscopy (XPS, Physical Electronics PHI 5600). Raman spectra were recorded with a Renishaw RM-1000 Micro Raman Spectrometer.  $\text{N}_2$  adsorption/desorption measurement was carried out by a Micromeritics ASAP 2020 instrument. The electrical conductivities were measured by sandwiching the cubic samples between two Pt foils through a two-probe method. An ICAP6300-type inductively coupled plasma (ICP) spectrometer (Thermo) was used to further analyze chemical compositions.

### 2.4. Electrochemical measurements

The as-synthesized HP-CF, Ma-CF, Mi-CM, and HP-CF@ $\text{NiCo}_2\text{S}_4$  were used directly as electrodes. Three-electrode measurements on these materials (used as the working electrode) were performed using the Pt plate, Hg/HgO electrode, and a 3 M KOH aqueous solution as the counter electrode, reference electrode, and electrolyte, respectively. Cyclic voltammetry (CV), galvanostatic charging/discharging (GCD), and electrochemical impedance spectroscopy (EIS) tests were conducted using a VMP3 electrochemical workstation (Bio-Logic) based on the mass of the whole working electrode. Symmetric supercapacitor (SC) devices were assembled by using two HP-CFs, a 3 M KOH aqueous solution, and a filter paper as symmetric electrodes, electrolyte, and separator, respectively. For the ASC, HP-CF@ $\text{NiCo}_2\text{S}_4$  and HP-CF@G- $\text{Fe}_2\text{O}_3$  served as the positive electrode and negative electrode, respectively. HP-CF@G- $\text{Fe}_2\text{O}_3$  was prepared by mixing G- $\text{Fe}_2\text{O}_3$  with polyvinylidene difluoride (PVDF), carbon black, and CNT at a weight ratio of 80:10:5:5 in N-methylpyrrolidone (NMP) and then coated onto a HP-CF with the equal mass, followed by vacuum

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