



# Porphyra derived hierarchical porous carbon with high graphitization for ultra-stable lithium-ion batteries



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## ABSTRACT

Hierarchical porous carbon was synthesized from porphyra using nickel nanoparticles as the template for mesopore formation and as a catalyst for carbon graphitization. The porphyra-derived carbon (PDC) showed a high degree of graphitization ( $I_G/I_D = 4.17$ ) and N-doping (5.32%). The reversible capacity of PDC was 1006.4 mAh/g at 0.1 A/g and 278.2 mAh/g at 5.0 A/g. Moreover, PDC demonstrated the reversible capacity of 520.8 mAh/g after 500 cycles at 1.0 A/g with 92.3% capacity retention rate. The PDC can be served as an advanced anode material for high-energy rechargeable lithium-ion batteries.

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## 1. Introduction

Carbon materials are prime candidates for applications in rechargeable lithium-ion batteries because (1) they undergo only 10% of volume change during lithiation, (2) have good cycle life, (3) demonstrate excellent electronic conductivity and (4) are very abundant [1]. Production of carbon from biomass is highly attractive and is considered a simple and economically feasible solution since raw materials are naturally available and renewable [2]. The current trends in carbonization of biomass are the synthesis of hard carbons (HC) with nanoscale pores for  $\text{Li}^+$  insertion and with the large surface area for  $\text{Li}^+$  adsorption. Because of these properties, HC has high capacity. Furthermore, because of naturally occurring nitrogen in biomass, it is easy to obtain from them N-doped carbonaceous materials with an increased amount of active sites and high lithium storage capacity [3]. However, disordered microarchitecture of HC leads to poor conductivity and unsatisfactory electrochemical cycling stability, which are fatal for batteries [4]. Many efforts have been undertaken to overcome these drawbacks of HC. Catalytic graphitization is a common method to introduce highly conductive and graphitic structures into HC [5] to ensure efficient ion diffusion and fast electron migration, both which provide sufficient storage sites to achieve high-capacity and stability during the energy storage.

In this paper, we demonstrate a very stable anode for Li-ion batteries based on biomass-derived carbon enhanced by catalytic graphitization. The synthetic strategy can provide an alternative method to make use of the algal that caused by the red-tide known as harmful algal blooms. Porphyra is a kind of wildly available algal, possessing the typical cellular structure and composition of algal, could be favorable for formation of hierarchical porous structures [6,7]. Moreover, porphyra contains sufficient amounts of polysaccharides and proteins. Proteins provide abundant N to achieve doped carbonaceous materials. Polysaccharides chelate with metal ions, which improves the dispersion of metal catalysts in carbon precursors and enhances catalytic graphitization [8]. We demonstrate that porphyra-derived carbons (PDC) with hierarchical porous structure, embedded graphitic carbon and N-doping offer enhanced capacity and cycling stability when realized as anodes in lithium-ion batteries (LIBs).

## 2. Experimental

Commercial porphyra was soaked in water to clean and to remove impurities. Then, 100 g of dried porphyra was immersed in 1000 mL of 10 wt%  $\text{Ni}(\text{NO}_3)_2$  solution for 24 h, then pulped by a blender and finally filtered and freeze-dried. The dried pulp was carbonized at 300 °C for 1 h followed by annealing at 800 °C for 2 h in Ar atmosphere. The carbonized porphyra was steam-activated at 800 °C for 1 h using a flow of 100 mL/min Ar carrier gas. The activated sample was washed with 20 wt%  $\text{HNO}_3$  to remove the residual nickel compounds. Finally, the residual black

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product was collected and dried. All characterization and measurements details of PDC are described in the [Electronic Supplementary Material](#).

### 3. Results and discussion

A sharp graphite peak in the PDS spectrum and an amorphous carbon peak were detected by X-ray diffraction (XRD, Fig. 1a). The peak at  $2\theta = 25.71^\circ$  is downshifted relative to the standard (002) peak of graphite at  $2\theta = 26.54^\circ$ . The interlayer spacing of graphite in PDC is 0.345 nm, which is larger than that of the regular graphite (0.335 nm). The peak around  $30^\circ$  belongs to another type of carbon (JCPDS 46-0943), which were commonly found in the chimney soot [9].

The intensity of the G band in the Raman spectrum of the PDC (see Fig. 1b) is significantly higher comparing to the D band (Fig. 1b), which indicates a higher degree of graphitization ( $I_G/I_D = 4.17$ ). The 2D Raman peak at  $2695\text{ cm}^{-1}$  is downshifted relative to the 2D peak of natural graphite ( $\sim 2726\text{ cm}^{-1}$ ), which suggests that the graphite embedded in PDC has a multi-layer structure. The well-developed graphitic structure can improve the electronic conductivity of the anode and maintain stability during charge/discharge cycling [10].

The  $\text{sp}^2\text{-C}$  (284 eV),  $\text{sp}^3\text{-C}$  (284.8 eV) and C–N (285.8 eV) peaks can be deconvoluted from the C1s spectrum of X-ray photoelectron spectra (XPS, Fig. 1c). Their percentages are 57.9, 19.2 and 22.9 at%, respectively. The high content of  $\text{sp}^2\text{-C}$  agrees with the presence of the high graphitic structure in PDC. The N1s spectrum (Fig. 1d) shows pyridinic N (398.2 eV), pyrrolic N (400 eV), graphitic N (401.2 eV) and nitro-typed N (405.7 eV). It is known that pyrrolic N and pyridinic N are active for electrochemical energy storage,

while graphitic N plays a significant role in improving electron transfer [11,12]. The abundant N-doping improves the capacity and conductivity of the PDC-based electrodes.

The scanning electron microscope (SEM) images of PDC have a multi-cellular structure (Fig. 2a) with many mesopores in the carbon walls (Fig. 2b). Transmission electron microscope (TEM) images (Fig. 2c) show a typical hierarchical structure. The dark areas correspond to the cellular frame; the bright areas are related to the porous structure. Graphitic carbon in PDC exhibits wrinkle-like structure with 5–10 layers (Fig. 2d). The size and shape of the multi-layer graphite are inherited from Ni nanoparticles, and the mesopores correspond to the sites, from which Ni particles were removed (Fig. S2a–b).

PDC nitrogen adsorption–desorption isotherms (Fig. S3a) show a combination of type I and type IV isotherm with a hysteresis loop at high relative pressure, indicating the co-existence of micropores and mesopores [13]. BET surface area of PDC is  $\sim 811.2\text{ m}^2/\text{g}$ . Pore-size distribution curves show two peaks at  $\sim 3$  and  $\sim 20\text{ nm}$  (Fig. S3b). The hierarchical porous structure can shorten the  $\text{Li}^+$  transport path and offer a large electrode/electrolyte interface for the charge transfer [14].

Fig. 3a shows cyclic voltammetry (CV) curves from 3.0 to 0.01 V at 0.1 mV/s scan rate. The apparent area centered at  $\sim 0.67\text{ V}$  was observed during the first discharge, which corresponds to the formation of the SEI layer [15]. The cathodic peak at  $\sim 1.6\text{ V}$  and an anodic peak at  $\sim 2.4\text{ V}$  were observed during the first CV cycle and then disappeared during the second cycle. The former peak corresponded to the reduction of oxygen of the C–O and C=O bonds and the later peak appeared due to Li binding with heteroatoms on the surface of the anode materials [10,16]. A long and flattened slope of the galvanostatic charge/discharge profile was

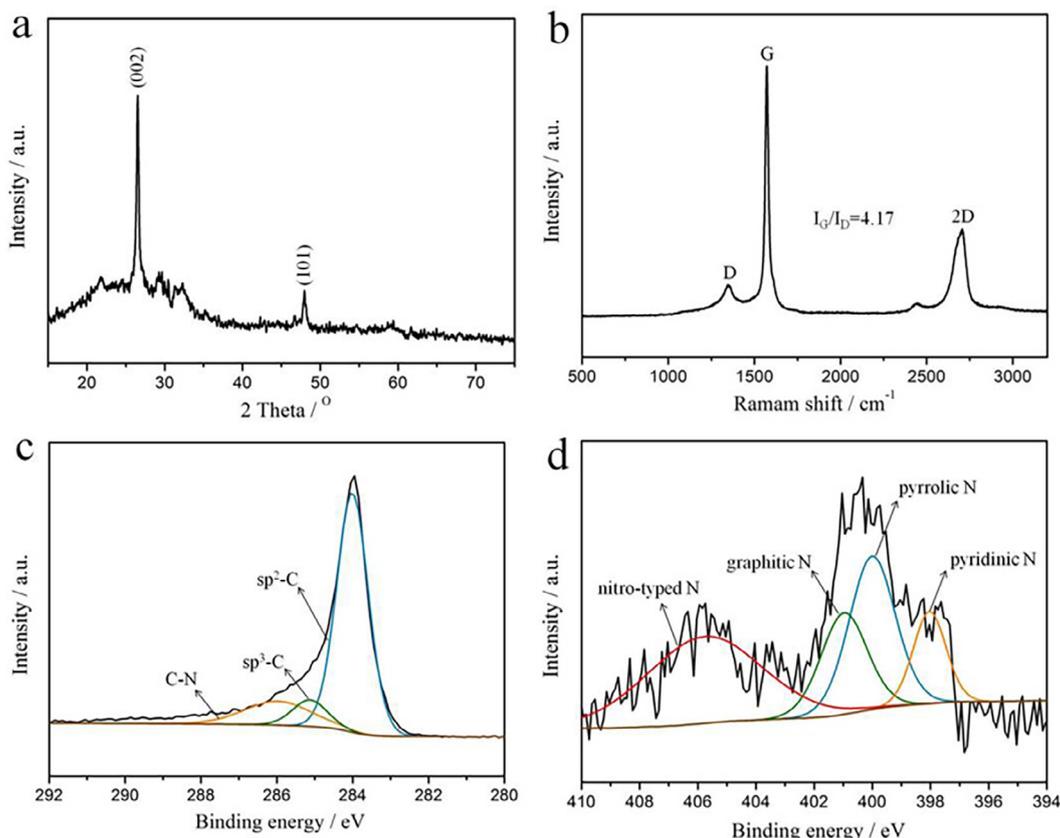


Fig. 1. (a) XRD pattern; (b) Raman spectrum; (c) C1s and (d) N1s XPS spectra of PDC.

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