



# Egg yolk-derived phosphorus and nitrogen dual doped nano carbon capsules for high-performance lithium ion batteries



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## ABSTRACT

Egg yolk-derived P and N dual doped nano carbon capsules (PNCCs) have been synthesized and used as lithium ion battery anodes. The application of egg yolk as the carbon source is a new and environmental-friendly approach for biomass recycling. The reversible capacity of half cells made of PNCCs is as high as  $\sim 770 \text{ mA h g}^{-1}$  at a current density of  $0.5 \text{ A g}^{-1}$  with considerable rate capacity and cycling stability. PNCCs show a capsule-like structure, which provide extra edges and active sites for lithium intercalation. The heteroatom doping also introduce defects and disorder, which increases the electrochemical activity and creates more active sites for lithium insertion.

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## 1. Introduction

Lithium ion batteries (LIBs) with high energy density, long cycle life, and satisfactory rate performance are among the most promising technologies for the development of electric vehicles and long lasting portable electronic devices [1]. In the past decades, graphite has been widely used as the anode material in LIBs due to its lithium intercalation capabilities, low operating potential versus lithium metal, and high stability [2]. However, graphite has several drawbacks including low storage capacity and limited rate capability in comparison to other carbon materials [3,4]. Recently, hollow carbon nanostructures including carbon capsules have been developed as promising candidates for LIB anodes, and have shown better electrochemical and mass transport capabilities in comparison to graphite due to their favorable structures for lithium intercalation and deintercalation [5–9].

Doping heteroatoms into carbon materials is another method to effectively tailor their intrinsic properties including the chemical features of surfaces and the electronic characteristics [10,11]. Due to the comparable atom size and different electronegativity

with carbon, N and P doping can modify the electron transport properties and improve the electrocatalytic activity of carbon materials. This approach has been used to enhance the capacity and cycling stability of LIBs [12,13].

Various research groups have also made carbon materials including carbon nanotubes, nanofibers, nanospheres, etc., for LIBs directly from biomass [14], including rice straws [15], and banana fibers [16]. However, to the best of our knowledge no studies have made carbon capsules from biomass and used them in batteries. Herein, we report for the first time a facile fabrication of N and P dual doped nano carbon capsules (PNCCs) using egg yolk as precursors. Besides from water ( $\sim 87\%$ ), egg yolks consist primarily of proteins ( $\sim 11\%$ , mainly composed of C, H, O, N, S), carbohydrate (1%), sugar (1%), and slight amount of minerals including Ca, Fe, Mg, P, K, Na, and Zn [17]. Applying egg yolk as the precursor naturally fits the requirements listed above. Moreover, considering that thousands of eggs are disposed every day due to the short expiration date, this method provides an approach for waste utilization. We found that PNCCs possess a capsule-like morphology with multiple graphitized carbon layers. We then applied PNCCs as the anode material for half-cell LIBs, where we evaluated the electrochemical performance of the LIBs in coin-type cells versus metallic lithium, showing a high specific capacity with high rate capability.

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## 2. Materials and methods

### 2.1. Preparation of PNCCs

We synthesized PNCCs in a facile method. As a first step, a normal chicken egg yolk bought from the supermarket was boiled and separated, and put into an HCl solution ( $6.0 \text{ mol L}^{-1}$ , 500 mL, Acros, 37% aqueous solution, diluted with deionized water). After that, we stirred the solution for 24 h at  $60^\circ\text{C}$  in order to ensure sufficient dispersion, and adjusted the pH to 5 using NaOH (Aldrich, 99.9%). We then added  $\text{Fe}(\text{NO}_3)_3$  ( $1.0 \text{ mol L}^{-1}$ , 200 mL, Sinopharm Chemical Reagent Co., Ltd, 99.5%) to the above solution in order to introduce  $\text{Fe}^{3+}$  ions. We further increased the pH to 6 by adding a citric acid buffer solution (Aldrich, 99.9%) in order to achieve a mild reaction environment and prevent precipitation. We centrifuged, washed, and subsequently dried the mixture in vacuum. As a second step, we heated the hydrolyzed yolk composite up to  $1000^\circ\text{C}$  under a  $\text{N}_2$  atmosphere for 45 min to form the desired PNCCs structure. The organic components decomposed into carbon and underwent certain degree of graphitization, while the N and P naturally present in the yolk were reduced and doped into the PNCCs. Meanwhile, the adsorbed  $\text{Fe}^{3+}$  ions were reduced into metal by carbon, subsequently nucleated and merged into bigger seeds. The Fe seeds further acted as the substrate for C precipitation and graphitization, forming the capsule-like carbon structure. Finally, we removed the encapsulated Fe metal by-product by HCl ( $4.0 \text{ mol L}^{-1}$ ) treatment for 12 h at  $80^\circ\text{C}$  so as to obtain the hollow structures. The proposed formation mechanism is illustrated in Fig. 1.

### 2.2. Basic characterizations

We characterized the morphology and structure of PNCCs by a high-resolution JEOL 2012 F transmission electron microscope (TEM). We examined the graphitization degree of PNCCs by an X'pert Pro PANalytical X-ray diffractometer (XRD) with a Cu  $K\alpha$  wavelength of  $1.5406 \text{ \AA}$ , and a Jobin Yvon HR 800 micro-Raman spectrometer at  $633 \text{ nm}$ . The elemental composition of PNCCs was studied by Physical Electronics PHI 5600 multi-technique X-ray photoelectron spectroscopy (XPS) system with Al monochromatic X-ray at  $350 \text{ W}$ .

### 2.3. Electrochemical measurements

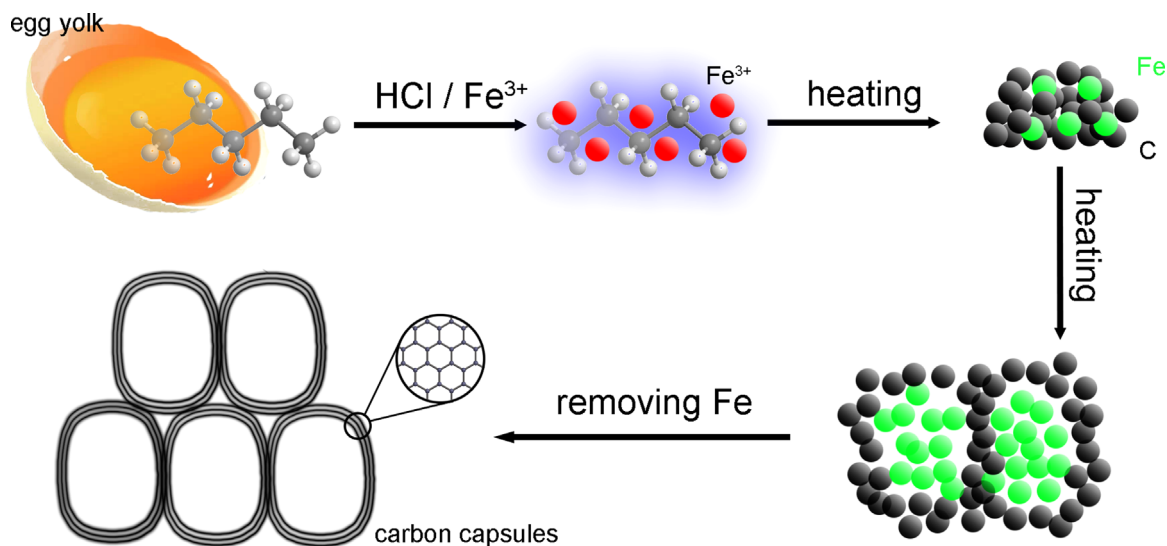
We carried out the electrochemical tests on a CR2032 coin-type cell assembled in a high purity argon glove box. The PNCC samples (90 wt%) were homogeneously mixed with polyvinylidene fluoride (10 wt%), pasted on a copper foil, and dried at  $120^\circ\text{C}$  in a vacuum oven to form the working electrode. We used a lithium plate as both counter and reference electrodes and a Celgard 2325 microporous polypropylene film as the separator. Ethylene carbonate and dimethyl carbonate (1:1 by volume) with  $1 \text{ mol L}^{-1}$   $\text{LiPF}_6$  served as the electrolyte. We tested the cells using an Arbin BT-2000 battery testing system at room temperature.

## 3. Results and discussion

### 3.1. Material characterization

Fig. 2(a) shows the overall morphology of the PNCCs sample. We can observe multiple hollow capsules with an average diameter of about  $60 \text{ nm}$ . This kind of multi-wall structure may be essential to the overall capacity [18]. Fig. 2(b) shows the structure of a specific PNCC. The thickness of the capsule shell is approximately  $10 \text{ nm}$  and has about 30 layers. A selected area of lattice fringes on the shell is magnified at the upper right with a layer distance of approximately  $0.335 \text{ nm}$ . This value is identical to the graphite interlayer distance, indicating that the carbon capsule is graphitic in nature.

We further examined the lattice structure of PNCCs via XRD as shown in Fig. 3(a). We found two characteristic peaks at  $26.3^\circ$  and  $45.5^\circ$ , corresponding to the (002) and (101) planes of hexagonal graphite respectively. The (002) plane at  $26.3^\circ$  corresponds to an interlayer distance of  $0.337 \text{ nm}$ , a value consistent with the fringe spacing of the TEM images. We attribute the relatively broad peak of (002) plane to the nano-scale multi-layered carbon shell structure, confirming that the PNCCs are thin shells possessing a high degree of graphitization [6]. Fig. 3(b) shows the Raman spectrum of PNCCs. The G-band at  $1590 \text{ cm}^{-1}$  is associated with the  $E_{2g}$  mode of graphitic carbon, while the D-band located at  $1352 \text{ cm}^{-1}$  corresponds to the defect induced mode [19]. The relatively high D-band peak and  $I_D/I_G$  value ( $\sim 0.79$ ) indicate that a certain amount of defects are present and that likely are a result of



**Fig. 1.** Schematic diagram of the formation process of PNCCs. Grey molecules represent the organic/inorganic composites from the egg yolk, and blue shadow means hydrolysis. Red, green, and black spheres are Fe ions, Fe atoms, and C atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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