



# Effects of copper nitrate addition on the pore property and lithium storage performance of hierarchical porous carbon nanosheets from phenolic resin



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## ABSTRACT

Hierarchical porous carbon nanosheets (HPCS) were prepared by using thermoplastic phenolic formaldehyde resin as the carbon source and copper nitrate as the template precursor. The effects of  $\text{Cu}(\text{NO}_3)_2$  loading content on the pore property and electrochemical performance of HPCS as anode material for lithium ion batteries were investigated. It was found that, with the addition of  $\text{Cu}(\text{NO}_3)_2$ , both the specific surface area and mesopore percentage increase. Correspondingly, the electrochemical performances of HPCS electrodes in terms of the specific capacity and rate performance improve for lithium ion batteries. The reasons were deduced and discussed from the view point of different pore size, especially the function of mesopores.

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## 1. Introduction

Lithium ion batteries (LIBs) have been widely used in various portable electronic devices like mobile phones, laptops, digital cameras and advanced medical devices, and also are being considered as promising energy storage devices for electric/hybrid vehicles and stationary electricity storage due to their high energy density, high voltage and long lifespan [1–4]. Graphite is the mainstay of anode materials for commercialized LIBs. But it possesses low capacity and the rate performance needs to be improved to satisfy the requirements for power LIBs. Although other electrode materials with high theoretical capacities such as Si, Sn and transition metal oxides have attracted broad attentions, they have the disadvantage of huge volume expansion during Li insertion and desorption [5,6]. Therefore, new carbon-based anodes with various microstructures have been widely investigated, such as graphenes [7], carbon nanotubes [8], carbon nanofibers [9], ordered mesoporous carbon [10], hollow structured carbon materials [11] and their composites [12,13]. Since the rate performance of LIBs is limited by the diffusion rate of Li-ions and the electron transport in electrode materials, many efforts have been paid to design different structures which would offer a high surface

area or a short diffusion distance to facilitate Li-ion transport [14,15].

Mesopores/macropores and hollow structures are in favor of promoting the high-rate performance of LIBs on the premise of not decreasing the electrical conductivity of carbon matrix by a large margin [16–20]. Up to now, a few reports have been referred to the performance improvement made by porous or hollow structures. For example, when micro/macroporous carbon monoliths were used as anode materials in LIBs, good electrochemical performance could be achieved as the large pore sizes may render electrolyte diffusion into the bulk of the electrode material facile and provide fast transport channels for Li-ions [21]. Lee and co-workers also found that millimeter-sized three-dimensionally ordered carbon monoliths with regular arrays of interconnected macropores showed much higher specific capacity at large current densities than similarly prepared non-templated carbon monolith [22]. Hollow carbon nanospheres with thin graphitic shells of about 10 nm and interconnected structure were prepared using zinc and sucrose. They exhibited a reversible capacity of 772 mAh  $\text{g}^{-1}$  at a rate of C/10 and good high-rate performance of 133 mAh  $\text{g}^{-1}$  at 10C because these nanopores and the hollow structure provide extra space for buffering the volumetric change during the Li insertion and extraction [11]. Although some reports described the enhancement of electrochemical performance by introducing porous or hollow structures to carbon anode materials for LIBs, few works analyzed the relationship between the pore structures (for example, the surface area and the ratio of different

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pores) of carbon materials and their lithium storage properties in detail.

In our previous work, hierarchical porous carbon nanosheets (HPCS) have been synthesized by introducing copper nitrate as template precursor [23]. HPCS exhibited a high specific capacity and favorable high-rate performance owing to the well-developed hierarchical pore system. Numerous mesopores and macropores reduced the solid-state transport lengths for Li-ion diffusion which is assumed to determine the overall rate. In this paper, we further investigate the influence of copper content on the pore structure and lithium storage performance to optimize the process and obtain valuable porous carbon anode materials for LIBs.

## 2. Experimental procedure

### 2.1. Synthesis of hierarchical porous carbon nanosheets

Thermoplastic phenolic-formaldehyde resin (300–500 polymeric units) as carbon source, copper nitrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , analytical pure grade) as metal source and hexamethylenetetramine were mixed in the Cu/C atomic ratio of 1/n ( $n=2, 4, 6, 8, 12, 16$ ). They were solidified at 150 °C for 4 h and carbonized at 600 °C for 6 h under the atmosphere of nitrogen. The obtained products were copper-embedded carbon nanosheets and then were oxidized by hydrogen peroxide (30%  $\text{H}_2\text{O}_2$ ) and acidified by hydrochloric acid (36.8%–38% HCl) to remove the copper nanoparticles. The final products, HPCS, were denoted as C-1-n. Based on the same procedure, the glassy carbon material (GC) was also prepared except no  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  addition.

### 2.2. Characterization

The morphologies and structures were examined by Hitachi H-800 transmission electron microscope (TEM) operating at 200 kV and JEOL-3010 high-resolution transmission electron microscopy (HRTEM). X-ray diffraction (XRD) experiments were carried out on Rigaku D/max-2500B2+/PCX system using Cu  $K\alpha$  radiation ( $\lambda=1.5406 \text{ \AA}$ ) over the range of 5–90° ( $2\theta$ ) at room temperature. Raman spectra were collected on Aramis (Jobin Yvon) using 532 nm laser excitation to compare the graphitization degree (ratio of D and G band of the carbon) of these samples. Nitrogen adsorption-desorption measurements were performed at -196 °C on ASAP2020 (Micromeritics, USA). The samples were degassed at 300 °C for 6 hours under a vacuum in the degas port of the analyzer before sorption measurement. Specific surface areas (SSA) were estimated according to the Brunauer-Emmett-Teller (BET) model, and pore size distributions were calculated by the Density Functional Theory (DFT) method.

### 2.3. Electrochemical measurements

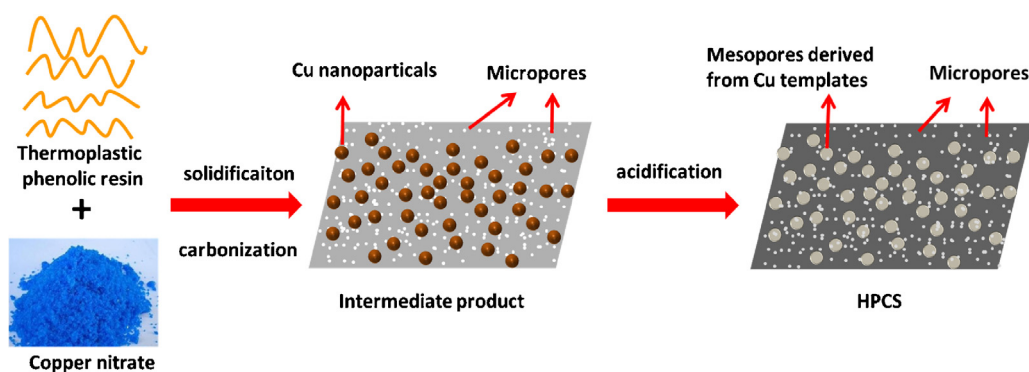
Electrochemical measurements were carried out using coin-type test cells (CR2032). The working electrodes were prepared by coating the mixture of active materials (HPCS and GC), acetylene black, and poly(vinylidene fluoride) (PVDF) (a weight ratio of 8:1:1) onto foam nickel. Pure lithium sheet was used as the counter electrode. The electrolyte consisted of a solution of 1 M  $\text{LiPF}_6$  in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 by volume). The cells were assembled in an argon-filled glove box (Unilab M Braun) in which both the concentrations of moisture and oxygen content were controlled to be less than 1 ppm. The electrochemical performance was tested at various rates in the voltage range of 0.01–2.50 V by Land CT2001A. The electrochemical impedance spectral (EIS) measurements were carried out on a CHI 660B electrochemical working station in the frequency range of 100 kHz to 10 mHz at the open circuit voltage of 1.8 V.

## 3. Results and discussion

### 3.1. Morphology and structure of HPCS

The formation of HPCS is briefly described in Scheme 1. A kind of carbon nanosheets with copper nanoparticles embedded in carbon matrix formed by solidification and carbonization. Micropores are produced owing to the escape of low-molecular gases from carbon matrix during carbonization. In addition, mesopores with corresponding size are obtained after the removal of copper nanoparticles. All these carbon materials prepared from phenolic resin- $\text{Cu}(\text{NO}_3)_2$  composites exhibit the nanosheet-type morphology with the thickness of about 40 nm shown in Fig. 1(a) and (b). The addition of copper nitrate could possibly alter the cross-linkage state of phenolic resin in the curing process and promote the generation of a layered carbon structure after carbonization [23]. The mesopores can be clearly seen on the carbon nanosheet surface (Fig. 1(c–f)), and with the increase of copper salt loading, the mesopore content increases. As illustrated in [23], the mesopores are derived from the Cu nanoparticles. It can be observed that the pore size on the nanosheets is about 20 nm in Fig. 1(c), 20–40 nm in Fig. 1(d) and (e), and 30–80 nm in Fig. 1(f). The size of mesopores from copper nanoparticles has an increased trend and the pore size distribution becomes widened with the increase of copper content. In addition, the pore size of C-1-2 is not as uniform as those of other samples which could be ascribed to the aggregation of copper nanoparticles and hence enlarged the corresponding mesopores.

Fig. 2(a) shows the XRD patterns of carbon nanosheets after the removal of copper nanoparticles. It can be seen that all the samples exhibit very broad and wide (002) peaks at  $2\theta \approx 23^\circ$ , lower diffraction angle compared with  $26.5^\circ$  for graphite, suggesting the



Scheme 1. The formation process of hierarchical porous carbon nanosheets.

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