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# Rape seed shuck derived-lamellar hard carbon as anodes for sodium-ion batteries

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Hard carbon with large interlayer spacing is suitable as the anode material for sodium-ion batteries. Rape seed shuck derived lamellar hard carbon is synthesized through hydrothermal and pyrolysis processes. As the anode, it exhibited good cycling stability, delivering a capacity of 143 mAh $g^{-1}$ after 200 cycles at 100 mA $g^{-1}$. The promising performances are attributed to the sheet structure with expanded interlayer distance (0.39 nm) and much void which can lower the sodium-ion insertion-extraction barrier and promote Na-ion diffusion and storage. The effect of pyrolysis temperature on the performance is also investigated.



## 1. Introduction

Due to the increasing demand of grid-scale energy storage and EV, the limit reserves of lithium require new alternative battery [1–5]. Abundant storage and the resemblance physicochemical property make sodium ion batteries (SIBs) as a promising alternative for LIBs [6–12]. Owing to the merits of environment benign, high electrical conductivity and stable structure of carbonaceous material, lot of investigation have been done, mainly includes carbon nanotubes [13–16], hollow carbon nanowires [17–19], carbon nanosheets [20,21] and carbon nanoparticles [22–24] and so on. However, preparing these carbons require expensive or non-renewable raw materials, and tedious preparation processes, which are disadvantage for large-scale industrialization production. By contrast, biomass precursors are very cheap, easy available can store Na-ions reversibly, which making biomass derived-carbon very potential as the anode of SIBs [25–28].

There are multifarious biomass precursors in the natural world, and they have varieties structure and texture. Through some suitable treatment processes, diversified porous structure could be obtained which have a positive effect on the electrochemical performance. For instance, a 3D connected porous carbon derived from pomelo peels synthesized by the simple pyrolysis of $H_3PO_4$-treated biomass had a high capacity of 181 mA h $g^{-1}$ after 220 cycles [29]; Anisotropic surfaces of leaf-dirved membrane with internal hierarchical porosity prepared by one-step thermal pyrolysis route delivered a specific capacity of 360 mAh $g^{-1}$ [30]; An enlarged nano-pores derived from holy leaf reported by hydrothermal followed high temperature pyrolysis process displayed a high capacity of 282 mAh $g^{-1}$ [31].

Rape seed shuck (RSS) is an agricultural residue. Every year, about 5 Mt of rape seed shuck is obtained and has been discarded [32]. This tremendous waste is rich in hemicellulose and cellulose fractions, which make it as a potential precursor for hard carbon. In this paper, a novel lamellar hard carbon was prepared through hydrothermal and high temperature pyrolysis carbonization process. As the anode of SIBs, it delivers an initial charge capacity of 237 mA h $g^{-1}$ at a current density of 25 mA $g^{-1}$, and 143 mAh $g^{-1}$ after 200 cycles at 100 mA $g^{-1}$. And we also investigate the effect of various pyrolysis temperature on the performance.

## 2. Experimental

### 2.1. Raw material

Rape seed shuck was locally collected after seed harvest from suburb farmlands of Shaanxi. The raw material was extensively washed with DI water, and dried at 110 °C overnight in a vacuum

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oven, milled using a laboratory crusher to a particle size smaller than 1 cm, homogenized in a single lot and stored until used.

### 2.2. Material synthesis

Typically, 2.0 g of rape seed shuck precursor was added into a 50 ml $HNO_3$ (10 wt%) solution under magnetic stirring for 30 min, the mixture was transferred into a 100 ml Teflon-lined autoclave in a homogeneous reactor at 180 °C for 24 h. After cooling down naturally, the precipitate was collected by filtration and washed thoroughly with deionized water and ethyl alcohol for several times. Eventually, the obtained products after hydrothermal process were carbonized at 500–800 °C under Argon atmosphere for 2 h (heating rate: 10 °C/min) with the flow of 50 sccm. The obtained was designated as RSS-X, where X represents the pyrolysis temperature.

### 2.3. Characterizations

The structures of the prepared samples were characterized by X-ray diffraction (XRD) using an X-ray powder diffractometer (Rigaku D/max-2200 PC). X-ray profiles were recorded between 10 and 80°(2θ) with Cu Ka radiation (λ = 1.5406 °A). The Raman spectra were recorded with a confocal microprobe Raman system (Renishaw-invia with a laser at 532 nm). Particle sizes, morphologies, and microstructures of the samples were observed by using a field-emission scanning electron microscope (FESEM, S-4800) with EDX and a transmission electron microscope (TEM, Tecnai $G^2$F20S-TWIN). Nitrogen adsorption/desorption isotherms were acquired at 77 K using a surface area and pore size analyser (NOVA 2200e). Specific surface areas were calculated based on the Brunauer-Emmett-Teller (BET) method. The Barrett-Joyner-Halenda (BJH) pore size distribution was determined from the desorption isotherms. A thermogravimetric analysis (STA409PC) was conducted at a ramp rate of 10 °C $min^{-1}$ to 1000 °C in $N_2$.

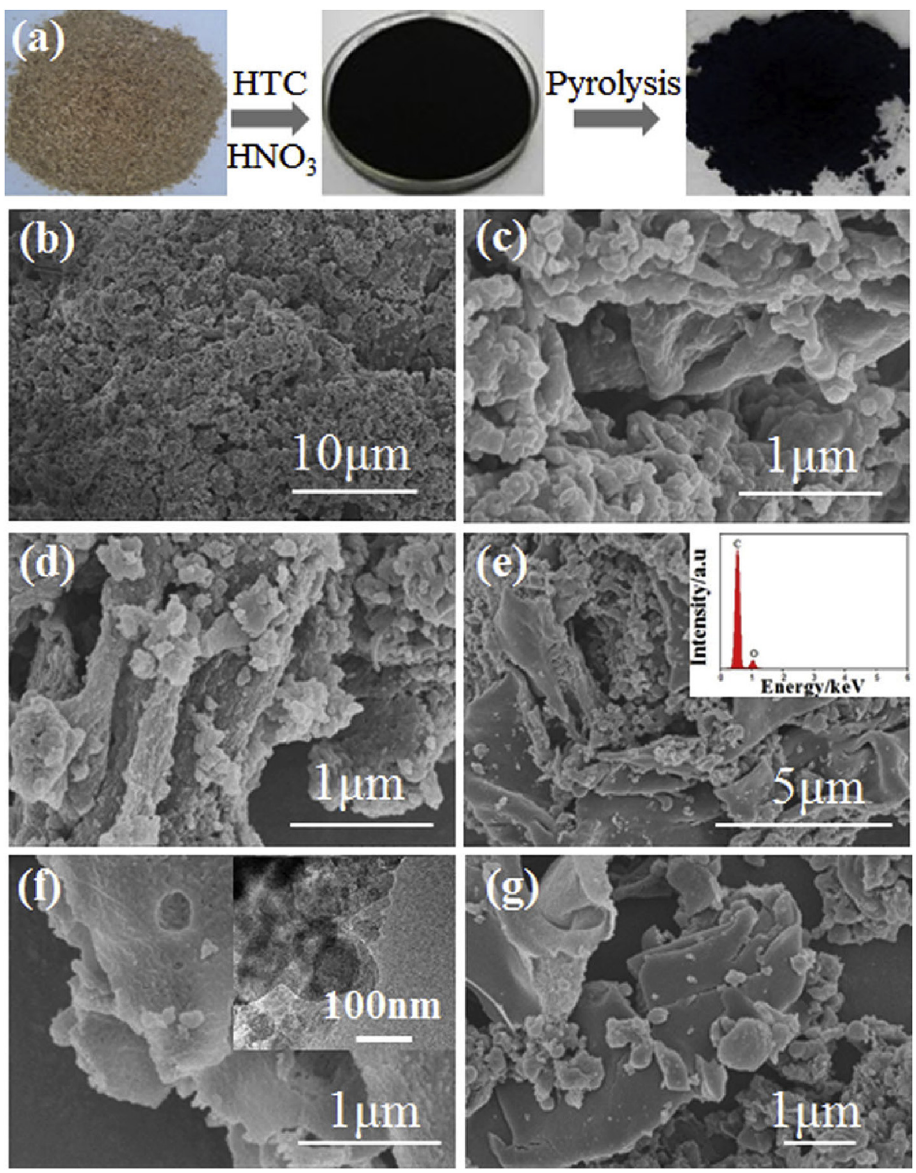


**Fig. 1.** The synthesis process of the derived lamellar carbon(a), SEM image of HTC (b), RSS-500 (c), RSS-600 (d), RSS-700 (e, f) and RSS-800 (g). The inset of Fig. 1e is the EDX of RSS-700. The inset of Fig. 1f is the TEM image of RSS-700.