



# The hierarchical cobalt oxide-porous carbons composites and their high performance as an anode for lithium ion batteries enhanced by the excellent synergistic effect



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## ABSTRACT

The designed metal oxide-carbon composites are always considered as a potential candidate for high-performance electrode materials. In this work, we fabricated the CoO rods-porous carbon composites with a unique hierarchical architecture by utilizing porous biocarbons derived from kapok fibers (KFs). As the composites of CoO nanocrystals with the mean size of 10 nm and graphene-like carbon sheets, the CoO rods are homogeneously anchored on or inside the porous carbons, thus achieving a 3D hierarchical porous structure. When tested as anode materials for lithium-ion batteries, the as-obtained composites exhibit the high lithium storage of 1057 mAh g<sup>-1</sup>. More importantly, the CoO rods/porous biocarbons composites display a superior long-term stable reversible capacity of about 550 mAh g<sup>-1</sup> at the high current density of 5 A g<sup>-1</sup> after 600 cycles. The superior electrochemical performance of the obtained composites has been attributed to the synergistic effect between CoO nanoparticles and porous biocarbons, which makes the composites favorable for fast electronic and ionic transfer, and superior stable structure. Therefore, we believe that the designed preparation of metal oxide architectures in low-cost and renewable porous biocarbons will be a valuable direction for exploring advanced electrode materials.

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## 1. Introduction

At present, the fast development of Li-ion batteries (LIBs) puts forward higher demands for advanced electrode materials and their large-scale preparing technology. As one key component of LIBs, the anodic materials are taken tremendous attention during the past decades [1,2], and so far amounts of new specimens have been explored and developed. Of them, transition metal oxides (TMOs) have been considered as one promising candidate due to their higher capacities than that of graphite [3–5]. Despite the marvelous features, TMOs are still hampered by the rapid capacity fading from drastic volume change and severe agglomeration as well as the low rate capability arising from poor conductivity. To overcome these drawbacks, combining TMOs with conductive carbons has proved to be a feasible approach [6–10]. In recent years, many successful examples including TMOs combined with graphene [8,11–16], CNTs [17], porous carbons [6,18], and so on

have been reported, which achieve the enhanced performance of anodic materials.

Compared to the expensive artificial carbons prepared through complex processes, several pioneering works by utilizing low-cost and renewable natural organism as carbon sources promote the fast-developing TMOs/biocalbon composites. At present, many biomass such as spirogyra [10], bamboo leaf [19], butterfly wings [20] and bacteria [21] and other low cost lignocelluloses materials have been explored to prepare composite electrodes, demonstrating the promising prospect in fabricating high-performance electrode materials. Inspired by it, our group paid considerable attention in recent years on fabricating new TMOs/C composites by utilizing various biomass as electrode materials of LIBs. Despite several expected composites with excellent electrochemical property have been obtained, numerous other tries are failed due to the poor porous features of biomass. As we all know, the porosity of electrode materials is one decisive factor on the diffusion speed of electrolyte ions and the reactive interface area, which can directly influence the electrochemical property of the samples. For example, many carbonaceous materials with hierarchically porous architecture exhibit superior high capacity and

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excellent rate property in contrast to common porous carbons [9,20]. Nevertheless, for most biocarbons, macropores are always dominant but less mesopores and micropores, which restrains greatly the performance enhancement of TMOs/biocalcarbon composites.

In recent years, many approaches to improve the porosity of biocarbons have been developed successfully by utilizing various activators and pore-expanding agents (such as KOH, ZnCl<sub>2</sub>, H<sub>3</sub>PO<sub>4</sub>) [22–25]. More and more highly porous carbons derived from various nature organisms have been reported [26–28], which exhibit much enhanced Li<sup>+</sup> storage performance. As one of current research hotspots, therefore, to design and fabricate novel nanostructures of TMOs supported by these porous biocarbons is attracting considerable attention. Herein, in this work we employed the activated porous biocarbons derived from kapok fibers (KFs) to create a new CoO rods/porous biocalcarbon composites (CoO/PBCs) through the hydrothermal and pyrolysis process. Due to the synergistic effect between CoO nanorods and highly porous carbons, the as-obtained CoO/PBCs composites exhibit the higher reversible capacity, and superior remarkable rate and cycling performance than previously reported CoO anode materials of LIBs.

## 2. Experimental sections

### 2.1. Preparation of materials

#### 2.1.1. Synthesis of porous KFs-derived biocarbons (PBCs)

KFs (mainly composed of cellulose, lignin, and xylan [29]) were first boiled in NaOH solution (95 °C) for 30 minutes to remove organic contaminants and create a hydrophilic surface. The cleaned KFs were immersed in 6 M KOH solution, and then dried at 100 °C for 12 h. The resulting samples were calcined in a tubular furnace under flowing argon at 750 °C for 1 h. After calcination, the products were washed with 2 M HCl solution and ultra-pure water until the pH value reaches to neutral, and then collected and dried.

#### 2.2. Synthesis of CoO/PBCs composites

Typically, 20 mg of the obtained PBCs were well dispersed in 24 mL deionized water by stirring for 30 min, and then 0.5 mmol of cobalt chloride (CoCl<sub>2</sub>·6H<sub>2</sub>O) and 2 mmol urea (CO(NH<sub>2</sub>)<sub>2</sub>) were dissolved into the above solution. After stirring to form a homogeneous solution, the solution was transferred into a 30 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 4 h. After cooling down to room temperature, the product was collected by centrifugation and washed with ultra-pure water, then the precursor was dried at 60 °C. In order to obtain the CoO/PBCs composites, the precursor was further annealed at 500 °C (3 °C min<sup>-1</sup>) for 2 h in argon flow.

For comparison, pure CoO nanoparticles were directly fabricated under the same procedure in the absence of KFs. Besides, the composite marked as PM-CoO/PBCs was synthesized by physically

mixing the pure CoO nanoparticles and PBCs according to the mass ratio in CoO/PBCs composites.

### 2.3. Material characterizations

The X-ray diffraction spectrographs analysis (XRD) was conducted on a German Bruker D8 Advanced X-Ray Diffractometer using Cu K $\alpha$  radiation. The morphologies of CoO/PBCs composites were characterized by field-emission scanning electron microscopy (SEM). The morphology of the synthesized composite was observed using transmission electron microscopy (TEM, JEM-2010). The thermogravimetric analysis (TGA) was examined on an SDT600 apparatus with a temperature ramp rate of 10 °C min<sup>-1</sup> from room temperature to 800 °C in air flow. The Raman spectroscopy was recorded on a Raman spectrometer (Raman, Jobin-Yvon Lab RAM HR800) with a radiation of 532 nm. The Brunauer-Emmett-Teller (BET) specific surface area and pore size distribution of the products were measured using a Belsorp-max surface area detecting instrument at 77 K.

### 2.4. Electrochemical measurements

The electrochemical measurements were conducted in two-electrode coin cell (CR2032) configuration. Working electrodes were fabricated by mixing the active material (CoO/PBCs), the conductive agent (carbon black) and the binder (PVDF) in N-methyl-2-pyrrolidone solvent at a mass ratio of 7:2:1. The mixture was uniformly spread on a copper foil that served as current collector and then cut into discs after drying at 120 °C in a vacuum oven overnight. The counter electrode was a lithium metal sheet and the separator was a polypropylene separator (Celgard 2400). 1 M LiPF<sub>6</sub> dissolved in the mixture of ethylene carbonate-dimethyl carbonate-diethyl carbonate (1:1:1 in volume) was regarded as electrolyte. The coin cells were assembled in an argon-filled glove box (H<sub>2</sub>O < 0.1 ppm, O<sub>2</sub> < 0.1 ppm), and electrochemical performance was evaluated on a Land Battery Measurement System (CT2001A) in the fixed voltage range between 0.05 V and 3 V vs. Li/Li<sup>+</sup> at room temperature. The cyclic voltammetry (CV) experiment was conducted at a scan rate of 0.1 mV s<sup>-1</sup> between 0.05 and 3.0 V on a Zahner Zennium electrochemical workstation. The electrochemical impedance spectroscopy (EIS) measurements were performed on a Zahner Zennium electrochemical workstation to measure impedance in the frequency range from 10<sup>-2</sup> to 10<sup>6</sup> Hz with an AC voltage signal of 5 mV. The open-circuit potential value of PBCs, CoO/PBCs, PM-CoO/PBCs and pure CoO electrode is 2.1 V, 2.2 V, 2.1 V and 2.2 V, respectively.

## 3. Results and discussion

The preparing procedure of CoO/PBCs composites is illustrated in Fig. 1. KFs are one kind of plant fibers, made of a mixture of lignin and cellulose. Despite KFs have the tube-like structure with the

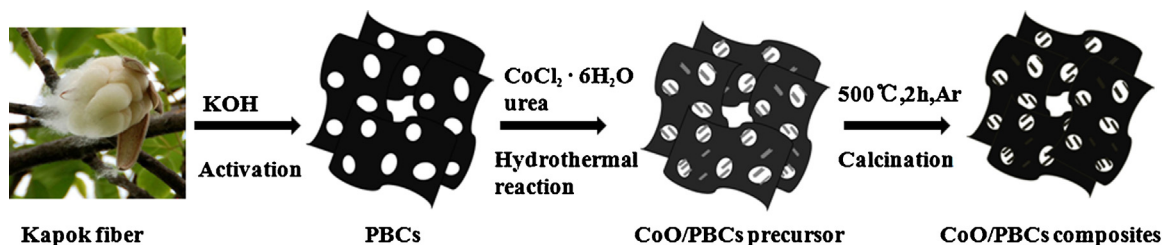


Fig. 1. Schematic illustration of the synthesis process of CoO/PBCs composites.

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