



# Fabrication of hierarchical cabbage-like carbonaceous materials by one-step cobalt-assisted hydrothermal carbonization of furfural



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## ABSTRACT

In this study, 3D hierarchical cabbage-like carbonaceous materials (CCMs) have been fabricated by one-step hydrothermal carbonization of furfural in the presence of cobalt acetylacetonate under mild condition. The morphologies and structures of the CCMs could be well controlled by regulating the reaction conditions including reactant concentration, reaction temperature and time. It was revealed that the cobalt acted as a structure-directing agent during the formation of the cabbage-like structures, which induced the morphology evolution of the products from microspheres into hierarchical CCMs. The good electrochemical performance and well-loading of Pt nanoparticles on the surface of the CCMs further indicated that the CCMs have potential applications in electrochemical capacitors and heterogeneous catalysis.

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## 1. Introduction

Current interest in carbonaceous materials with novel micro/nanostructures is inspired by their extensive potential applications in adsorbents, catalysts, and electrochemical capacitors [1–3], etc. In particular, the three-dimensional hierarchical carbonaceous materials, such as hollow spheres [4], porous structures [5], cross-linked nanofibers [6], flowerlike structures [7] have attracted considerable attention, due to their excellent physicochemical properties which could be improved or even endowed by the complex morphologies and structures [5,8–10]. Hence the research for fabrication of carbonaceous materials with novel hierarchical structures has become a hot topic.

Among various strategies for synthesis of carbonaceous materials, the hydrothermal carbonization (HTC) has been considered as a promising technique to prepare novel carbonaceous materials from simple carbohydrates, owing to its more sustainable, practical and low-cost characteristics [11–15]. However, effective adjustment of the hierarchical and various structures of hydrothermal carbonaceous materials is still challenging, although many researches have been reported to prepare controllable carbonaceous

structures by regulating the reaction conditions of HTC, such as reaction time and temperature, solvents, templates or surfactants, and so on [8,16–20]. This problem is mainly due to the mild hydrothermal conditions. Interestingly, it was worth noting that metal substances have significant influence on the morphologies and structures of carbonaceous materials. Zhang et al. reported mono-dispersed ellipsoidal carbon microparticles were obtained in the presence of Cu foil, however, substituting Cu with Al or Cr, the main products were microballs rather than the ellipsoids [21]. Moreover, it was reported that the metal microparticles with special structures could be employed as the templates to prepare hierarchical carbonaceous architectures [22–24]. For example, Huang and his coworkers have prepared the three-dimensional flower-shaped composites using the prepared flower-shaped ZnO as a template [23]. However, this synthetic method generally required more than two steps including the preparation of structured metal-templates and then formation of hierarchical carbon/metal particles. Furthermore, it has been demonstrated that the metal ions also could be used as metal-precursors to assist the fabrication of novel carbonaceous structures via HTC [25–28]. Yu et al. found that both hollow and massive carbon microspheres could be obtained in the presence of Fe<sup>2+</sup> ions, whereas the presence of Fe<sub>2</sub>O<sub>3</sub> nanoparticles leading to a very fine, ropelike carbon nanostructure [26]. Titirici and coworkers synthesized the hierarchical porous

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carbonaceous materials via ionothermal carbonization of carbohydrate precursors with the assistance of [Bmim][FeCl<sub>4</sub>] [28]. All of the mentioned literatures above suggested that the metal ions could play a key role on the formation of carbonaceous materials with special morphologies and structures. Therefore, it is essential to further develop a conceivable, facile and one-step strategy by combining the effect of metal ions with HTC technique to fabricate the novel and hierarchical carbonaceous structures.

In this paper, the 3D hierarchical cabbage-like carbonaceous materials (CCMs) have been synthesized by one-step cobalt-assisted HTC under mild conditions, using cobalt acetylacetonate (Co(acac)<sub>2</sub>) as a metal precursor, and biomass derivative-furfural as carbon precursor. No any surfactant and template were employed in this process. A typical cabbage-like spherical structure is composed of sheet-like building units intersecting each other. Various functional groups were presented on the surface of the CCMs, which improved the hydrophilicity and stability of the CCMs in aqueous systems. Based on the effect of the reaction conditions on the morphologies and structures of the products, a possible formation mechanism of the CCMs was proposed. The electrochemical performance of the activated CCMs was investigated. In addition, the hierarchical CCMs was also used as the supports of melt nanoparticles for synthesis of heterogeneous catalysis.

## 2. Experimental

### 2.1. Synthesis of the CCMs

The typical synthesis of the 3D CCMs was carried out as follows: 0.2–0.9 g of cobalt acetylacetonate (Co(acac)<sub>2</sub>, Adamas Reagent Co. Ltd) and 40 mL of distilled water were put into a beaker. Then, 1 g of furfural (Sinopharm Chemical Reagent Co. Ltd) was added with stirring until a homogeneous solution was obtained. The resulting solution was transferred into a stainless steel autoclave with capacity of 60 mL, then sealed and heated at 180 °C for 16 h. After that, it was cooled to room temperature. The obtained dark precipitate was collected and separated by centrifugation. Then the acquired solid products were washed repeatedly with deionized water and absolute alcohol. After drying the resulting products at 60 °C for 12 h, the CCMs were successfully prepared. The prepared CCMs were heated to 400 and 700 °C with N<sub>2</sub> atmosphere and maintained for 3 h, respectively. The obtained products were named CCMs-400 and CCM-700 correspondingly.

### 2.2. Synthesis of the Pt-CCMs

The Pd-CCMs were prepared in the following way [29]. 0.1 g as-prepared CCMs powder was added to 20 mL distilled water and sonicated for 10 min till the CCMs samples were completely dispersed in solvent. The mixture solvent as part A. 0.1 g SnCl<sub>2</sub> (Tianjin Chemical Reagent Co. Ltd) was dissolved in 20 mL HCl dilute solution as part B. Parts B was added to Parts A and stirred for 20 min. Then washing repeatedly with water by centrifugation, and the recovered precipitate was dispersed into 20 mL distilled water. 15 mL of H<sub>2</sub>PtCl<sub>6</sub> (Aladdin Chemistry Co. Ltd) was added to above solution and stirred for 20 min. And then, 15 mL of hydrazinehydrate (Tianjin Chemical Reagent Co. Ltd) (0.05 g 80% hydrazinehydrate diluted with 15 mL distilled water) was added slowly in drops to the above mixture solution under stirring. After stirring for 2 h, the as-prepared suspension was separated by centrifugation and the recovered precipitate was washed three times with distilled water. The products were dried under vacuum at 60 °C overnight. Thus the Pt-CCMs catalyze were obtained.

### 2.3. Characterization

The morphologies of the products were examined by a scanning electron microscopy (SEM, FEI Quanta 200) operating at 15 kV. Samples for SEM were prepared by spreading the dispersion of products on aluminum foil, then sputter-coating with gold powder. Transmission electron microscope (TEM, FEI Tecnai F20) equipped with an energy dispersive X-ray spectrometer (EDX, EDAX Inc) were performed at an accelerating voltage of 200 kV. Samples for TEM were prepared by supporting product dispersion on copper grids. The particle size was measured on dynamic light scattering (DLS) with angle detection at 90°. The Fourier Transform Infrared (FTIR) spectrum was recorded on a Magna-IR 560 instrument (Nicolet, USA), and the samples were prepared by tableting with KBr. The X-ray photoelectron spectroscopy (XPS) analysis was carried out in K-Alpha X-ray photoelectron spectra (Thermo Fisher Scientific Co. Ltd, USA) with the vacuum chamber pressure of  $5 \times 10^{-7}$  Pa. The X-ray diffraction (XRD) pattern was recorded with D/MAX 2200 diffractometer equipped with a rotating anode and a Cu-K $\alpha$  source ( $\lambda = 0.15406$  nm). Raman spectrum was recorded on the DXR Raman Microscope (Thermo Fisher Scientific Inc.) with an excitation wavelength of 532 nm. The nitrogen adsorption–desorption isotherms were measured on a Quantachrome Autosorb AS-1 instrument. Pore size distributions were obtained using the Barrett–Joyner–Halenda (BJH) model.

### 2.4. Electrochemical measurement

The working electrode was prepared by mixing 80 wt.% as-prepared material, 10 wt.% carbon black and 10 wt.% polytetrafluoroethylene in ethanol and then coated onto the nickel foam with a coating area of 1 cm<sup>2</sup>. The coated nickel foam was dried at 80 °C for 8 h and then pressed under a pressure of 10 MPa. The three-electrode system was performed with platinum foil and Hg/HgO electrodes as counter and reference electrodes, respectively. Both the CV and galvanostatic charge–discharge curves were recorded on a CHI720D electrochemical workstation in 6 M KOH aqueous electrolyte. CV test was carried out between –1.0 and 0 V with different scan rate. Galvanostatic charge–discharge was test was performed in the same potential range with the current densities ranging from 0.5 to 10 A/g. The specific capacitance was calculated using following equation:

$$C = (I\Delta t)/(m\Delta V)$$

Where C (F g<sup>-1</sup>) is the specific capacitance, I (mA) is the discharge current, and m (g),  $\Delta V$  (V) and  $\Delta t$  (s) represent the mass of electroactive material, the voltage drop upon discharge and the total discharge time, respectively.

## 3. Results and discussions

### 3.1. Morphology and structure

The morphology and structure of the CCMs obtained at 180 °C for 16 h were investigated studied by SEM and TEM (Fig. 1). As shown in the low-magnification SEM image (Fig. 1a), it can be seen that the products consist of uniform cabbage-like particles with an average size of about 4  $\mu$ m without aggregation, indicating that the mono-dispersed CCMs could be obtained under this reaction condition. The overall morphology of the individual particle could be clearly observed from high-magnification SEM image (Fig. 1b), which shows the 3D hierarchical cabbage-like structure composed of sheet-like building units with the thickness of about 150 nm. It should be noted that the microstructure of the CCMs consisted of

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