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Fabrication of carbon microspheres with controllable porous structure by using waste *Camellia oleifera* shells

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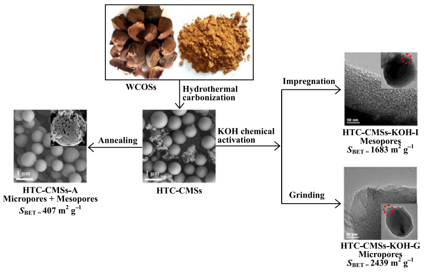
HIGHLIGHTS

- Porous carbon microspheres were fabricated from waste *Camellia oleifera* shells.
- Their morphology, textural property, and composition were well characterized.
- Fabrication mechanisms of spherical and porous microstructures were elucidated.

GRAPHICAL ABSTRACT



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ABSTRACT

Carbon microspheres with controllable porous structure were directly fabricated from waste *Camellia oleifera* shells through hydrothermal carbonization combined with physical activation or KOH chemical activation technique. The morphology, textural property, and compositional and structural information of as-prepared carbon materials were well characterized. The as-prepared aromatic carbon microspheres exhibit a perfectly spherical structure under carefully controlled hydrothermal carbonization conditions, whereas the as-prepared porous carbon microspheres feature a large surface area and a controllable porous structure. Subsequently, the porous carbon microspheres obtained by KOH chemical activation were successfully applied to the quick removal of phenolic organic pollutants from water. In addition, this paper further elucidated the mechanisms underlying the fabrication of spherical microstructure and controllable porous structure through hydrothermal carbonization of waste *Camellia oleifera* shells and pore-fabricating technique.

1. Introduction

Development and application of carbon materials is important in various fields, such as catalytic materials, adsorbents, gas and energy storage, electrode materials, carbon fuel cells, and biochemicals [1–7]. Nevertheless, carbon materials produced using non-renewable resources are not conducive for sustainable development. Sustainable carbon materials directly prepared from waste crude plant materials through hydrothermal carbonization have provided new opportunities and challenges in the science of carbon materials [8–12].

Camellia oleifera shells, which are agricultural waste from the production of camellia oil, contain four main ingredients, including cellulose, hemicellulose, tea saponin, and lignin [13–16]. Large

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amount of waste *Camellia oleifera* shells (WCOSs) are produced every year in China, which can only be treated through combustion, resulting in serious environmental pollution and resource waste. The conversion of high amounts of WCOSs to carbon materials through hydrothermal carbonization will provide significant scientific, economic, and environmental benefits.

Carbon microspheres, an important member of the carbon material family, can be applied as functional material supports, fillers for high-performance liquid chromatography columns, preparation templates for core/shell or hollow structures, and anode materials for lithium-ion batteries [17–21]. Carbon microspheres are prepared through traditional methods, including chemical vapor deposition, pyrolysis, and solvothermal treatment by using chemicals (e.g., asphalt, polycyclic aromatic hydrocarbons, and polypropylene) and high-quality biomass (e.g., glucose, sucrose, starch, and cellulose) as raw materials [22–25]. Nevertheless, these methods and materials used to prepare carbon microspheres present limitations, such as complex operation procedures, damage to the environment, and high cost, and are therefore unfavorable for large-scale industrial production. The fabrication of carbon microspheres through hydrothermal carbonization by directly using crude plant materials, such as sugar beet chips, pine cones, pine needles, oak leaves, and orange peels, is an advantageous approach for market development [26–30]. The fabrication of high-quality carbon microspheres by directly using crude plant materials and determining the underlying formation mechanism are two main tasks that must be addressed.

Porous carbon materials have been the focus of research because of their special surface physical and chemical properties, such as large surface area, adjustable pore size, and abundant surface active groups [31–34]. Porous carbon materials have been widely applied to energy storage materials, anode materials for lithium-ion batteries, carbon dioxide separation and capture, and chemical separation [35–42]. Annealing and KOH chemical activation are two simple and effective methods used to prepare porous carbon materials. Nevertheless, the construction of a controllable porous structure into the framework of carbon microspheres while maintaining the integrity of the spherical structure requires precise control of the annealing and KOH chemical activation conditions.

In this work, high-quality carbon microspheres were directly fabricated using WCOSs as raw materials by carefully controlling the hydrothermal carbonization conditions. Only water was used as a reaction medium in the hydrothermal carbonization process, thereby rendering the preparation process as cheap and environment friendly. The formation mechanism of carbon microspheres was studied through component separation of WCOSs and gas chromatography/mass spectrometry (GC-MS) analysis of the hydrothermal reaction solution. A controllable porous structure was fabricated into the framework of as-prepared carbon microspheres through annealing or KOH chemical activation, and the underlying fabrication mechanism was elucidated. Subsequently, the porous carbon microspheres prepared by KOH chemical activation were applied to the quick removal of phenolic organic pollutants from water.

2. Experimental

2.1. Fabrication of aromatic carbon microspheres directly from WCOSs through hydrothermal carbonization

WCOSs were collected from Jiangxi Green Sea Oil Co. Ltd., China. Crude WCOSs were dehydrated, crushed, and then passed through a 200-mesh sieve to prepare WCOSs powder. The powder was directly used to fabricate high-quality carbon microspheres by carefully controlling the hydrothermal carbonization conditions. Briefly, 2.0 g of the WCOSs powder was uniformly dispersed in 60 mL of deionized water by using a 500 W ultrasonic crasher for 1 h, with a 1:30 mass ratio of the WCOSs powder to water. The resulting suspension was stirred for 6 h at room temperature and then subjected to hydrothermal treatment at 230 °C for 12 h at a heating rate of 1 °C/min. The byproducts of the hydrothermal carbonization reaction were removed through Soxhlet extraction and ultrasonic–microwave synergistic extraction by using water as solvent. After drying at 60 °C for 24 h, the final products were obtained and denoted as HTC-CMSs. The percent yield of HTC-CMSs is 33.01% with respect to WCOSs. For comparison, various HTC-CMSs samples were prepared by using the same method but with reduced hydrothermal carbonization temperature (120 °C), shortened (6 h) and prolonged (18 h) hydrothermal carbonization time, inadequate (1:50) and excessive (1:10) mass ratio of WCOSs powder to water, continued agitation, and selecting cellulose, hemicellulose, tea saponin, and lignin separated from WCOSs as raw materials.

2.2. Fabrication of carbon microspheres with controllable porous structure through physical activation or KOH chemical activation

Carbon microspheres with controllable porous structure were fabricated through annealing, KOH impregnated activation, or KOH grinding activation. For annealing, 0.5 g of HTC-CMSs was annealed at 650 °C for 2 h under argon atmosphere with a heating rate of 5 °C/min. The obtained products were denoted as HTC-CMSs-A. The percent yield of HTC-CMSs-A is 56.15% with respect to HTC-CMSs. For KOH impregnated activation, 0.5 g of HTC-CMSs was uniformly dispersed in 6.7 mL of 5.4 mol/L KOH solution by using a 500 W ultrasonic crasher for 10 min. The mass ratio of HTC-CMSs to KOH is 1:4. After vigorous stirring at room temperature for 12 h, impregnated HTC-CMSs were obtained by filtration and drying at room temperature in a Petri dish. The impregnated HTC-CMSs were subjected to thermal treatment at 650 °C for 2 h under argon atmosphere with a heating rate of 5 °C/min. The final products were obtained after washing with water to neutral pH and denoted as HTC-CMSs-KOH-I. The percent yield of HTC-CMSs-KOH-I is 43.62% with respect to HTC-CMSs. For KOH grinding activation, 0.5 g of HTC-CMSs and 2.0 g of KOH were mixed by grinding in a mortar. The mass ratio of HTC-CMSs to KOH is 1:4. The HTC-CMSs/KOH mixture was subjected to thermal treatment at 650 °C for 2 h under argon atmosphere with a heating rate of 5 °C/min. The final products were obtained after washing with water to neutral pH and denoted as HTC-CMSs-KOH-G. The percent yield of HTC-CMSs-KOH-G is 25.32% with respect to HTC-CMSs.

2.3. Characterization

Field-emission scanning electron microscopy (FESEM) images were recorded using a JEOL JSM-6700F microscope, whereas transmission electron microscopy (TEM) images were recorded on a JEOL JEM-2010 microscope at an accelerating voltage of 200 kV. Nitrogen gas porosimetry measurements were performed on a Quantachrome NOVA 2000e surface area and porosity analyzer after the samples were outgassed under a vacuum at 70 °C for 20 min and 150 °C for 6 h, respectively. X-ray diffraction (XRD) patterns were obtained using a Panalytical X'Pert PRO diffractometer via Cu Kα radiation with the 2θ angle scanning range of 10–65°. Fourier transform infrared (FTIR) spectra were recorded on a Bruker VERTEX 70 FTIR apparatus. Raman scattering spectra were recorded on a PerkinElmer RamanStation 400F spectrometer equipped with 350 mW 785 nm near-infrared laser source and RamanMicro 300 microscope. Thermogravimetric (TG) and derivative thermogravimetric (DTG) analyses were conducted under N_2