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# Facile fabrication of hollow and honeycomb-like carbon spheres from liquefied larch sawdust via ultrasonic spray pyrolysis

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ABSTRACT

The facile fabrication of hollow and honeycomb-like carbon spheres from liquefied larch sawdust by ultrasonic spray pyrolysis has been reported. The morphology and porous structure of the carbon spheres are investigated. The cross-linked spherical morphology observed at 700 °C breaks down above 800 °C. The size of the obtained carbon spheres increases from 600 to 900 nm at 5% solution concentration to 0.6–1.5 μm and 0.6–2.0 μm at 10% and 15%, respectively. The optimal carbon spheres prepared with 5% solution concentration and 800 °C possess a honeycomb-like structure, uniform size (600–900 nm) and narrow pore size distribution (1.8–2.5 nm). The well-developed porous structure and uniform size distribution can endow the carbon spheres with high methyl orange adsorption capacity (140 mg/g).





## 1. Introduction

Carbon spheres (CSs) have attracted considerable attention in adsorbent, catalyst supports and energy storage owing to their high surface area, tunable porous structure and excellent chemical and physical properties [1]. Recently various approaches, including self-assembly template [2], pyrolysis [3] and hydrothermal synthesis [4], have been used to prepare different types of CSs. However, these methods are potentially expensive, experimentally complex and dangerous, which limits their industrial applications. Thus, a facile strategy for the preparation of CSs is desirable. Ultrasonic spray pyrolysis (USP) as a promising method is effective to generate carbon spheres using a nebulizer and tubular furnace. It is suitable for the continuous production of light-weight spherical particles from low-volatility precursors; the particles are rapidly carbonized and collected to obtain the CSs [5,6].

In general, the porosity of the CSs prepared by USP largely depends on the precursors. The most common precursors are resins [7] and metal oxides [8]. However, increasing energy and environmental demands have driven the development of renewable resources. Owing to their high availability and renewable characteristic, biomass materials such as waste wood are widely used to prepared carbon materials. However, it is difficult to directly synthesize CSs from wood. The liquefaction technology can effectively convert lignocellulose into low molecular chemicals, which can be used to prepare CSs. In this study, we use liquefied larch sawdust as the carbon precursor for the preparation of novel CSs via USP. The roles of solution concentration and carbonization temperature in the formation of CSs and the performance of the carbon spheres for methyl orange adsorption are investigated systematically.

## 2. Materials and methods

### 2.1. Preparation of liquefied larch sawdust

According to the reported literature [9], larch sawdust (10 g), phenol (30 mL), sulfuric acid (98%, 1 mL) and phosphoric acid (85%, 2 mL) were mixed. Then the mixture was heated under reflux at 110–120 °C for 1 h. After that, methanol (100 mL) was added to the liquefied product for filtering. And the pH of the mixture was adjusted to neutral for further filtering to remove the precipitate. The filtrate was concentrated by vacuum distillation at 40 °C to yield liquefied larch sawdust, which was diluted to produce different solution concentrations (5%, 10% and 15%).

### 2.2. Synthesis of carbon spheres using UPS

The as-synthesized liquefied larch sawdust solution was transformed into light-weight and hollow droplets in an ultrasonic device, followed by carbonization at different temperatures. The samples were isolated by centrifugation and dried overnight at

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90 °C. The obtained samples were denoted as CS-*x*-*y*, where *x* was the concentration of the liquefied larch sawdust solution and *y* was the carbonization temperature.

### 2.3. Characterization

The morphology and size of the CSs were observed using a scanning electron microscopy (SEM) and field emission scanning electron microscopy (FESEM). For the preparation of samples, a few CSs powers sticking in the conductive adhesives were fixed on the apparatus. The porous structure was observed by transmission electron microscopy (TEM). The porous structure was characterized by $N_2$ sorption isotherms at −196 °C using a Micromeritics ASAP 2020 instrument.

### 2.4. Methyl orange (MO) adsorption test

Methyl orange was dissolved in deionized water and then diluted to the required concentration before use. Then the carbon spheres (0.01 g) were introduced in 10 mL MO solution and continuously shaken at 25 °C for 12 h. The suspension was filtered for detecting the solution concentration using a UV–vis spectrophotometer at 361 nm.

## 3. Results and discussion

The SEM images of CSs are represented in Fig. 1a-I–e-I. The CSs possess a honeycomb-like morphology formed from the degradation of cellulose and lignin during the carbonization process [10]. The FESEM images (Fig. 1a-II–e-II) of CSs show that CSs are hollow and have thin shells, which results from the rapid transfer of the solution into small and hollow drops [5]. At the fixed concentration of 5%, the CSs with a uniform size of 600–900 nm are formed. The cross-linked morphology of the CSs occurred at 700 °C (Fig. 1a-I–a-II), which results from the incomplete degradation of the precursors. As the increase in carbonization temperature to 800 °C, the CS-5-800 (Fig. 1b-I–b-II) has the well-dispersed and honeycomb-like spherical morphology. However, the spherical morphology breaks down at 900 °C (Fig. 1c-I–c-II). This is because high carbonization temperature may lead to a breakdown of aligned structural domains in the carbon matrix. The results reveal that the carbonization temperature has a significant effect on the morphology of the CSs. In addition, the concentration of the liquefied larch sawdust solution can modify the size of the CSs. The CS-5-800 has a uniform size range of 600–900 nm. With an increase in the solution concentration to 10%, the size of the CSs increases to 0.6–1.5 μm (Fig. 1d-I–d-II). For the CS-15-800 (Fig. 1e-I–e-II), a size range of 0.6–2.0 μm is obtained. These results are ascribed to the easy core growth of CSs at high solution concentration. The well-defined spherical morphology and uniform size range are optimized at 5% of the liquefied larch sawdust solution and 800 °C. The TEM images of the optimal carbon spheres show a typical disordered porous structure (Fig. 1f-I–f-II).

Fig. 2a shows the nitrogen sorption isotherms of the obtained CSs. The CSs exhibit a mixed I–IV isotherm with steep adsorption below the $P/P_0$ of 0.1 indicating the formation of abundant micropores and typical $H_2$ hysteresis loop at the $P/P_0$=0.4–1 that is associated with capillary condensation in the mesopores [11,12].

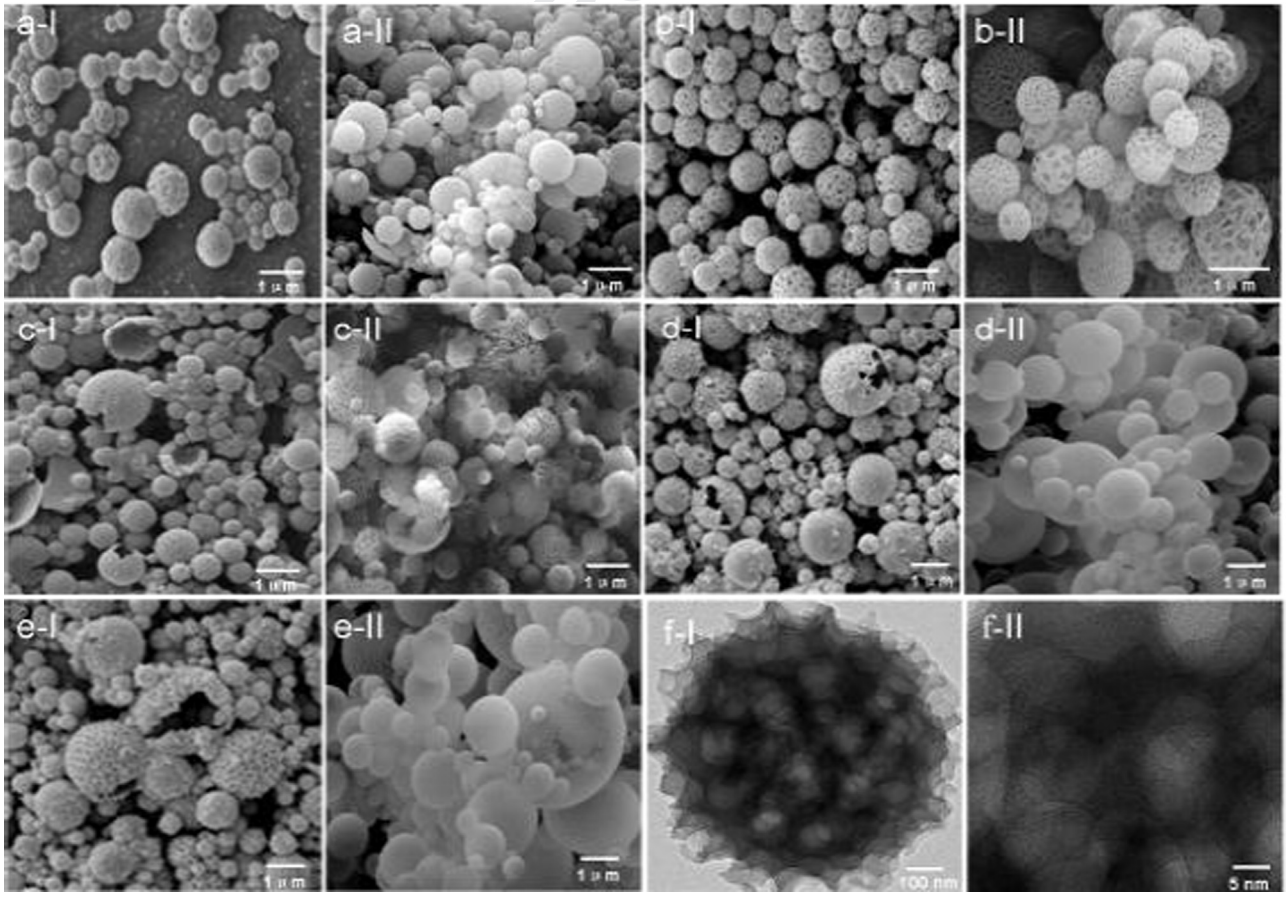


**Fig. 1.** SEM images of CS-5-700 (a-I), CS-5-800 (b-I), CS-5-900 (c-I), CS-10-800 (d-I), and CS-15-800 (e-I). FESEM images of CS-5-700 (a-II), CS-5-800 (b-II), CS-5-900 (c-II), CS-10-800 (d-II), and CS-15-800 (e-II) TEM images of CS-5-800 (f-I, f-II).

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