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Coupled soft-template/hydrothermal process synthesis of mesoporous carbon spheres from liquefied larch sawdust

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ABSTRACT

Mesoporous carbon spheres (CSs) with tunable morphology and pore structure were prepared from liquefied larch sawdust by coupling the soft-template and hydrothermal methods. The morphology and size of the CSs could be controlled by changing the concentration of F127 (PEO–PPO–PEO), and the pore structure could be tuned by changing the carbonization temperature. The results showed that perfect CSs were achieved when the concentration of F127 was 6%. The morphology changed from spherical to raspberry-like and the particle size decreased with increasing F127 concentration. The pore structure transformed from spiral-like, to vermicular-like, to wave-like as the carbonization temperature was increased. In contrast, the pore size showed a decreasing tendency under the same conditions. The adsorption capacity of CSs for Mn (II), Cd (II), Pb (II) and Cr (III) increased with increasing of carbonization temperature. The adsorption capacity of CSs for removal Pb (II) can reach 75%.

1. Introduction

Mesoporous carbons with desired morphologies, adjustable pore size, and tunable pore structure have received considerable attention, and show great promise for applications [1,2]. Recently, several strategies have been reported for the rational design of mesoporous carbons with a spherical morphology [3], is that carbon spheres (CSs). Among the various possible methods, coupling the soft-template method with the hydrothermal process has been shown to have powerful capabilities in controlling the synthesis of carbon materials with spherical morphologies [4]. A major challenge for these approaches is the choice of precursor. The most commonly used precursors are furfuryl alcohol and phenolic resin [5,6], which are typically produced from fossil resources, or are synthesized chemically. Considering the large quantity and renewable characteristics of biomass such as waste wood, the transformation of waste wood to give mesoporous CSs seems promising. However, the carbonization of wood cannot involve a melting step. It is difficult to prepare carbon materials with a regular morphology and a controlled porous structure directly from wood.

The liquefaction of wood with phenols has proven to be an effective approach for converting lignocellulosic materials into low molecular weight chemicals. The obtained liquid products can be used as feedstock for the synthesis of phenolic resin [7]. Our previous report showed that liquefied birch sawdust can be used as a carbon source for the preparation of carbon foams with honeycomb and network structures [8].

Here, we report the simple synthesis of stable mesoporous CSs, using larch sawdust as a cheap precursor and F127 (PEO–PPO–PEO) as soft-template. And, we used different concentrations of F127 to control the spherical morphology, and different carbonization temperatures to control the pore structures.

2. Experimental

Larch sawdust (10 g), phenol (30 mL), sulfuric acid (98%, 1 mL), and phosphoric acid (85%, 2 mL) were added into a three-necked glass reactor and heated under reflux at a temperature of 110–120 °C for 1 h. The mixture was filtered and the pH was adjusted to neutral and filtered again. The filtrate was concentrated using vacuum distillation at 40 °C, giving the liquefied larch sawdust.

In a typical synthesis, formaldehyde (37%, 90 mL) and sodium hydroxide (3 g) were added to liquefied larch to generate larch-based resin. Different concentrations of F127 (3%, 6%, 8%, and 10%) were added to the liquefied larch and stirred for 12 h at 40 °C, following adjustment of the pH to 0.5 and performed for 12 h. The reaction mixture was allowed to react for 6 h at 180 °C. The mixture was then carbonized under a N_2 atmosphere at different temperatures (500 °C, 600 °C, 700 °C) for 2 h. The resultant CSs were denoted as CS-*x*-*y*, where *x* was the concentration of F127, and *y* was the carbonization temperature.

The morphology of the CSs was examined using scanning electron microscopy (QUANTA200) operating at an accelerating voltage of 15 kV. Transmission electron microscopy images were

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obtained on a JEOL 2011 instrument operated at 200 kV. Nitrogen sorption isotherms were investigated using a Micromeritics ASAP 2020 using nitrogen as the adsorbate, at 77 K. Before analysis, all samples were degassed at 300 K for more than 10 h. Measurement of the adsorption capacity of Mn (II), Cd (II), Pb (II) and Cr (III) from an aqueous solution was carried out as follows. 0.1 g of CSs sample was added to Mn (II), Cd (II), Pb (II) and Cr (III) solutions (25 ml) with concentrations to 4 mg/mL. The bottles were sealed with paraffin film and then shaken for 12 h at 30 °C, at a frequency of 150 strokes min^{-1}. The amount of Mn (II), Cd (II), Pb (II) and Cr (III) adsorbed was evaluated using atomic absorption spectroscopy (TAS-990).

3. Results and discussion

The CS-6-non hydrothermal-700 sample appeared as spherical vesicles (Fig. 1a); because the block copolymer F127 had amphiphilic properties, the hydrophilic groups allowed the formation of spherical micelles, while the hydrophobic cores provided an ideal location for encapsulation [9]. In fact, the synthesis of the CSs began with cores of F127 in the resin matrix, and the cores subsequently grew and connected as the matrix was heated [8]. The CS-6-700 sample (Fig. 1c) exhibited spherical structures with a size of approximately 10–25 μm. This indicated that the hydrothermal method optimized the spherical morphology via dehydration, condensation, and polymerization. In the CS-3-700 sample (Fig. 1b), few spheres appeared, and the particle size ranged from 2 to 10 μm. In contrast, in CS-6-700 (Fig. 1c), some spherical carbon particles were formed, and the particle size ranged from 10 to 25 μm. These phenomena might have been observed because 6% was the critical micellization concentration. When the concentration of nuclei reached a critical saturation point, crystal nuclei formed and grew as the surface-reactive functional groups on the larch resin intermediate product diffused and adsorbed on their surfaces; as they grew, connections were made between the crystal nuclei, and they grew until the carbon microspheres were finally formed [10]. With increasing copolymer concentration, the size of the obtained carbon spheres decreased (3 μm), but aggregation occurred (Fig. 1d). This indicated that N_{agg} (the power of aggregation) was essential for inducing the assembly. Increase in N_{agg} resulted from decrease in the chain length [10]; under these conditions, the spheres aggregated to a significant degree, and their size decreased. When the F127 concentration was increased to 10%, the spherical particles still aggregated (Fig. 1e). These aggregates formed raspberry-like structures with a particle size of approximately 2 μm. This may have been due to the fact that the polymer chains had to adopt new arrangements to reduce their core chain length beyond the critical micellization concentration. These results indicated that the morphology and size could be tuned by controlling the concentration of F127.

Because the F127 copolymer templates could be decomposed at 250–400 °C under N_2 [11], a mesoporous structure was obtained. The pore structure could be controlled by using higher carbonization temperatures [3]. CS-6-500 showed a spiral-like porous structure. This might have been due to the formation of pentagonal structures as the micelles and phenolic resin first polymerized; the positive curvature in these structures caused the formation to grow in a skewed fashion, resulting in the formation of a porous screw structure with nitrogen protection at 500 °C (Fig. 2a) [12]. With increased temperatures, the original pore structure surface was covered with growths of disordered graphite-layer tablets; this meant that the carbon-layer arrangement increased, and the spiral-like porous structure changed to give a vermicular-like porous structure (Fig. 2b) [13]. When the carbonization temperature was increased further, the graphite layer was composed of an intermittent, denser, wave-like porous structure. This was because the degree of graphitization improved, and the space between the graphitic layers decreased (Fig. 2c) [10].

The as-synthesized CSs typically showed intrinsic porous structures when higher carbonization temperatures were used. Fig. 3 shows the nitrogen sorption isotherms and the pore size distribution curves for CSs obtained at different carbonization temperatures. The nitrogen sorption isotherms for the samples were type IV; a hysteresis was observed over the P/P_0 range of 0.45–0.9. The sharpness of the hysteresis loops did not change, which was associated with the occurrence of capillary condensation in the mesopores, caused by the decomposition of the F127

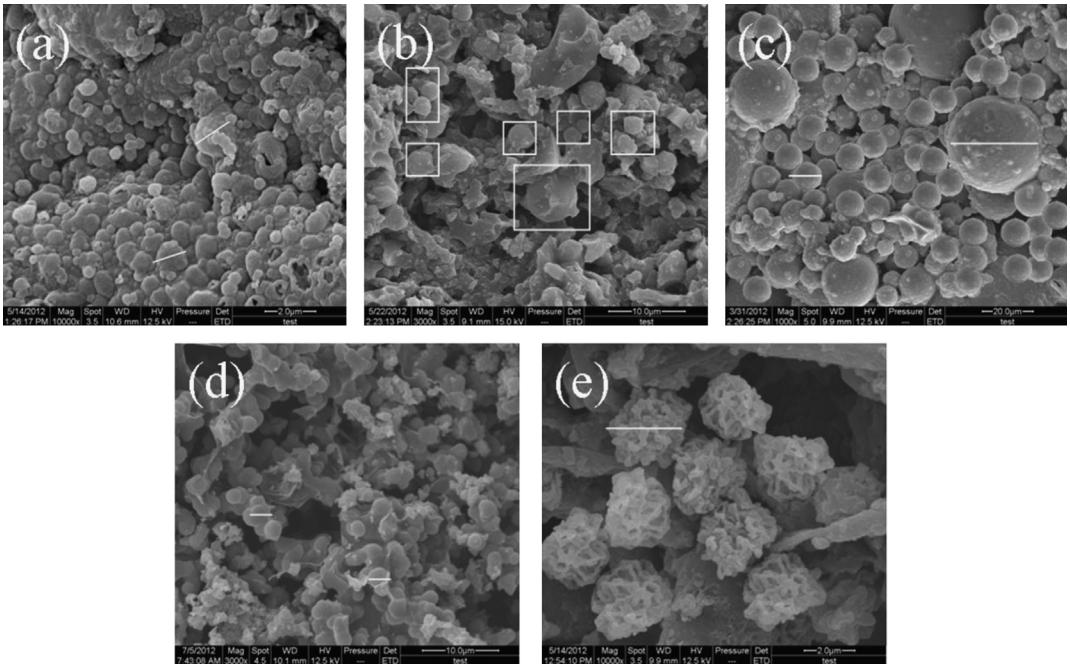

Fig. 1. SEM images of the CSs samples prepared under different conditions (a: CS-non hydrothermal-700; b: CS-3-700; c: CS-6-700; d: CS-8-700 e: CS-10-700).