Study on the preparation of pressure-assisted monodisperse carbon spheres

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Abstract

Strictly controlling the particle size and monodispersity of hydrothermal carbon spheres (HCSs) is the key and difficult point in the preparation process. In this study, a simple and chemical-additive-free method was developed, that is, external pressure assisted hydrothermal carbonization of glucose to prepare HCSs. The effect of external pressure on the particle size, number of surface functional groups and monodispersity of HCSs was investigated. The photothermal conversion performance of HCSs was investigated, and the photothermal conversion effects of HCSs with different particle sizes were compared. The results show that without external pressure, the average particle size of HCSs was 1021 nm, and the particle size distribution was extremely uneven. When the external pressure was 2.0 MPa, the average particle size of HCSs was 89 nm, and the uniformity was significantly improved. FTIR and XRD results all indicated that the external pressure only affected the particle size and the number of surface functional groups of HCSs, but did not change the chemical structure of HCSs.

Keywords

External pressure assisted, hydrothermal carbonization, carbon spheres.

1. Introduction

Glucose hydrothermal carbon spheres (HCSs) are widely used in catalysts or catalyst supports [1-2], adsorption materials [3-4], chromatographic column materials [5], supercapacitors [6-7], sacrificial templates [8-9], biomedicine [10] and other fields due to their regular spherical morphology, adjustable particle size, and stable chemical structure. They are also ideal models for basic research in colloidal science. Monodispersity is a key challenge in the preparation of HCSs and a prerequisite for studying the size effect of HCSs. According to the size of HCSs, they can be divided into carbon microspheres (particle size >1 μm) Carbon micro nanospheres (particle size 100 nm-1μm) , and carbon nanospheres (particle size 20-100 nm) [11]. Carbon nanospheres, due to their smaller particle size and abundant surface functional groups, are more conducive to surface modification or direct application [12].

However, the traditional hydrothermal method for preparing HCSs has two major problems: poor monodispersity and difficulty in reducing particle size. The methods to solve the problem of monodispersity mainly include seed method and the method of adding dispersants. The seed method refers to the selection of carbon nanospheres (~93 nm) [13] or polystyrene spheres (PS spheres) [14] as seeds, which can prevent the generation of new carbon nuclei during the preparation process and improve the monodispersity of HCSs. But this method increases the preparation steps and production costs. Another preparation method is to add an appropriate amount of sodium polyacrylate [15] or poly (4-styrene sulfonic acid maleic acid copolymer) sodium salt [16] as a dispersant to obtain HCSs with uniform particle size by inhibiting the formation of new carbon nuclei. But this method will introduce impurities, increasing the difficulty of subsequent cleaning. This article proposes the use of external pressure assisted hydrothermal method to prepare HCSs with controllable particle size and excellent monodispersity. This method only increases the initial pressure on the basis of traditional hydrothermal method to avoid the introduction of impurities and simplify the preparation process.

2. Experimental part

2.1. Preparation of pressure Hydrothermal Carbon Spheres，PHCSs

Dissolve 4.5 g of D-glucose in 50 mL of deionized water and stir for 30 minutes until the solution is colorless and transparent to ensure its uniformity. The stirred glucose solution is placed in a autoclave with a 100 mL polytetrafluoroethylene lining. Connect the air inlet valve of the autoclave to the nitrogen cylinder, inject 1.0-3.0 MPa nitrogen (99.9%), and the pressure in the autoclave can be read directly through the pressure gauge. After holding at 180 ℃ for a period of time, cool to room temperature. The obtained black brown solid was washed several times using anhydrous ethanol/deionized water as the cleaning agent through ultrasonic dispersion and centrifugal collection until the cleaning agent became colorless. Finally, it was dispersed and stored in a 50 mL aqueous solution.

2.2. Testing and Characterization of HCSs

The morphology of HCSs was observed using scanning electron microscopy (SEM, TESCAN) and field emission scanning electron microscopy (FESEM, feveris460). The crystal structure was determined using an X-ray diffractometer (XRD, Bruker D8) with a Cu-K light source. The surface functional groups were determined using Fourier transform infrared spectroscopy (FTIR, Bruker Vertex 70). The particle size and distribution were measured by dynamic light scattering (DLS). The laser wavelength was 633 nm and the scattering angle was 173 °. The carbon structure was determined using ^{13}C solid-state magic angle rotation (MAS) nuclear magnetic resonance (NMR, Agilent 600M) spectroscopy. The visible near-infrared spectra of HCSs were obtained using a UV Vis NIR (Cary 5000) spectrophotometer.

3. Results and discussion

3.1. SEM and DLS analysis

The morphology and particle size distribution of HCSs prepared under different conditions are shown in Figure 1. The particle size range of THCSs is wide, ranging from 200 nm to 2.2 μ m. This indicates that the monodispersity of HCSs prepared by traditional methods is poor, which is consistent with previous research results [13]. With the introduction of external pressure, the particle size uniformity of PHCSs significantly improves. When the external pressure is 1.0 MPa, the PDI decreases to 0.379 (Figure 1B and b), and the particle size range narrows. When the external pressure increases to 2.0 MPa, the PDI decreases to 0.08 (Figure 1C and c), indicating that PHCSs exhibit excellent monodispersity under this pressure. When the applied pressure increases to 3.0 MPa, PHCSs adhere (Figure 2A), which may be due to the further compression of the solution volume (Figure 2B) as the applied pressure continues to increase. The distance between PHCSs decreases and the collision probability increases, ultimately leading to the occurrence of adhesion. Therefore, an external pressure of 2.0 MPa is the most suitable pressure in this article.

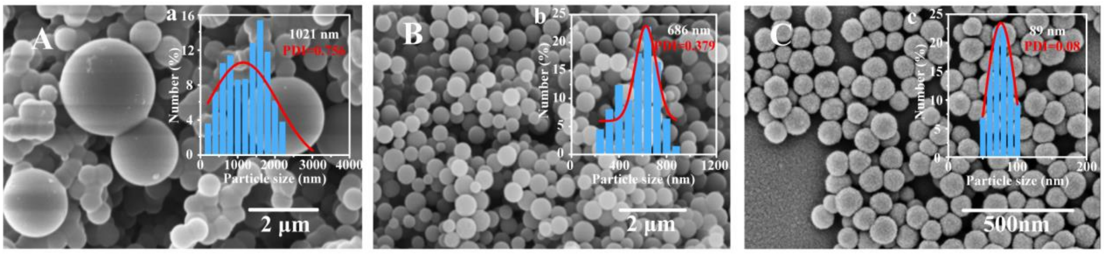

Figure 1: SEM and DLS plots of (A) THCSs, (B) PHCSs 1.0 MPa, and (C) PHCSs 2.0 MPa

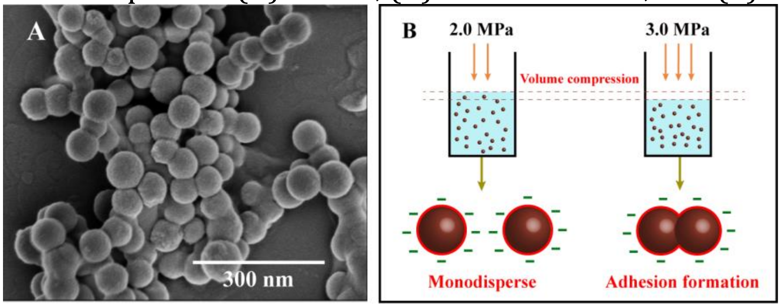

Figure 2: (A) SEM image of PHCSs-3.0 MPa, (B) Schematic diagram of PHCSs-3.0 MPa adhesion

3.2. FTIR and XRD analysis

The surface oxygen-containing functional groups of THCSs and PHCSs at 2.0 MPa were characterized using FTIR, as shown in Figure 3A. The characteristic peaks at 3473 cm^{-1} and 1108 cm^{-1} correspond to the stretching and bending vibrations of O-H, the characteristic peaks at 2927 cm^{-1} and 2852 cm^{-1} correspond to the stretching vibrations of fat CH, and the characteristic peaks at 1705 cm^{-1} and 1622 cm^{-1} correspond to the stretching vibrations of C=O and C=C [17]. Comparing the infrared spectra of THCSs and PHCSs at 2.0 MPa, it can be seen that both surfaces contain a large number of oxygen-containing functional groups (such as -OH, -C=O, and -COOH), and the applied pressure does not change the type of THCSs functional groups.

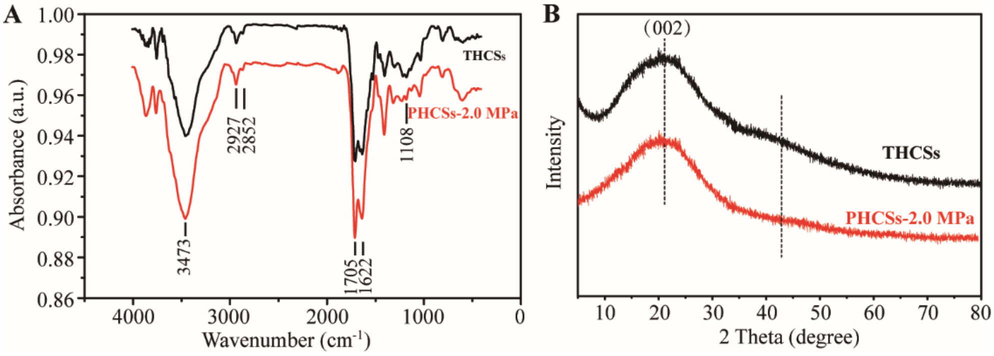

Figure 3: (A) FTIR and (B) XRD spectra of THCSs and PHCSs at 2.0 MPa

The crystallinity of THCSs and PHCSs 2.0 MPa was analyzed using XRD, as shown in Figure 3B. The strong and wide peaks of 15-30 ° belong to the (002) crystal plane, indicating that both materials are composed of amorphous polycyclic aromatic carbon sheets. The weak peak of 40-45 ° belongs to the (101) crystal plane, indicating that the degree of graphitization of the two materials is very low [14,18]. Comparing the XRD spectra of THCSs and PHCSS-2.0 MPa, it can be seen that external pressure does not affect the crystallinity of THCSs.

4. Conclusion

We have innovatively developed a method for preparing PHCSs using glucose hydrothermal carbonization assisted by external pressure. External pressure can effectively improve the monodispersity of PHCSs, with a PDI of 0.08 when the external pressure is 2.0 MPa. Continuing to increase the pressure will cause adhesion of PHCSs. Therefore, 2.0 MPa is the most suitable pressure in this study.

Acknowledgments

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