



## Original Research Paper

## Preparation of mono-dispersed carbonaceous spheres via a hydrothermal process

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## ABSTRACT

Mono-dispersed carbonaceous spheres (CS) with a narrow size distribution were synthesized via hydrothermal treatment of glucose. The effects of hydrothermal temperature and time, glucose concentration and pH value of solution were investigated in detail. Structures and surface properties of as-prepared products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), Induced coupled plasma emission spectroscopy (ICP), thermogravimetric analysis/differential scanning calorimetry (TG/DSC), Nitrogen adsorption/desorption and Fourier transformed infrared spectroscopy (FTIR). The results showed that the production yield of CS increased from 2.1 to 32% with increasing the temperature from 160 to 180 °C, and the average size increased from 0.23 to 0.95 μm with extending the hydrothermal time from 8 to 16 h. pH value of the starting solution showed an evident effect on the morphology of CS via affecting the decomposition products of glucose. CS could be obtained when the pH value of starting solution was less than 12, but further increasing the pH value to 13–14 led to the formation of lumpy aggregations of carbon rather than spherical CS. The CS prepared under pH 6 and 9 showed good adsorption capacity for Methylene blue (MB), which was attributed to their relatively high specific surface area.

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## 1. Introduction

Carbonaceous spheres (CS) are extensively used in many areas, such as in high strength carbon-based materials [1–3], catalyst supports [4], templates [5,6] and secondary lithium ion rechargeable batteries [7], owing to their high surface energy, controlled size and morphology [8], high thermal conductivity and high compressive strength [9].

A variety of techniques have been used to synthesize CS, including chemical vapor deposition (CVD) [10,11], emulsion process [12,13], chemical pyrolysis [14] and template method [15]. However, all these techniques suffer various disadvantages, such as complicated operation process, use of toxic precursors, and low carbon productivity. Hydrothermal process [16–19] has advantages of low cost, mild preparation condition and non-necessities of organic solvents, surfactants and catalysts, and thus becomes one of the most important methods for CS preparation. Liu et al. [18] prepared CS via a hydrothermal process, and investigated

the effects of the hydrothermal parameters, including the concentration of glucose solution, reaction temperature, duration, and the second hydrothermal treatment. Their results revealed that 4–5 h hydrothermal treatment at a temperature between 180 and 190 °C was suitable for CS formation and the size of CS increased with increasing the concentration of glucose. Mono-dispersed CS with good morphologies and large numbers of oxygen containing functional groups (primarily –OH and C=O) were obtained at 190 °C for 4 h using a 0.3 mol/L glucose solution. Romero-Anaya et al. [20] prepared CS at 180–240 °C for 12–48 h by using a hydrothermal method, and showed that with extending the reaction time from 12 to 24 or 48 h, CS with better morphology could be synthesized and their average size increased from 0.72 to 5.8 μm with increasing the glucose concentration from 0.8 to 1.6 mol/L.

Although a number of previous studies have investigated the effects of different processing parameters, such as hydrothermal temperature, time, and solution concentration on the hydrothermal process of glucose, and the morphology and size of CS, their effects on the CS production yield are not fully understood. In addition, the effects of another important processing factor, the solution pH, on the CS morphology and size [21], and on the overall

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CS preparation process remain unclear. Therefore, in this work, all of these will be addressed in detail.

## 2. Experiment

### 2.1. Raw materials and sample preparation

Glucose ( $C_6H_{12}O_6 \cdot H_2O$ , AR; Bodi chem. Co. Ltd. Tianjin, China) and Methylene bluetrihydrate ( $C_{16}H_{18}ClN_3S \cdot 3H_2O$ , Sinopharm chem. Co. Ltd. Shanghai, China) were used as the main starting materials. A typical preparation process for CS is described as follows: a glucose solution with a given concentration and pH value was prepared initially (the pH value was adjusted by using 0.1 mol/L HCl and 0.1 mol/L NaOH solutions), and subsequently subjected to autoclaving at different temperatures for different time periods. Since the hydrothermal process is a closed high pressure reaction, the reactor pressure increases with the reaction temperature. For security and energy saving reasons, a series of CS were hydrothermally prepared at 160–200 °C in the present paper. After the completion of reaction, the solution was cooled to room temperature, and the black precipitates were collected and washed with deionized water and ethanol to remove residual by-products. The production yield is defined as the mass ratio of the products obtained from the hydrothermal process to the initially used glucose. The resultant black product was dried at 80 °C for 12 h. The detailed processing conditions are listed in Table 1.

### 2.2. Adsorption experiments

The adsorption isotherms of as-prepared samples were investigated using methylene blue (MB) as an adsorbate. Typically, 200 mg of the sample powders were added into 50 mL MB aqueous solution with concentration ranging from 0 mg/L to 50 mg/L contained in a beaker. The suspension was then homogenized using a magnetic stirrer at 288 K for 30 min. After centrifugation, the concentration of dye solution was measured using a UV–visible spectrophotometer.

The adsorption kinetics of as-prepared CS was also examined. Typically, 600 mg of as-prepared CS were added to an MB aqueous solution (150 mL, 30 mg/L) in a beaker. The suspension was then mixed using a magnetic stirrer of 150 rpm at 288 K, and 10 mL suspension was periodically taken from the reactor after each pre-determined time interval and centrifuged to measure the dye concentration using a UV–vis spectrophotometer, the maximum adsorption wavelength of 665 nm of MB was used for calculation.

The equilibrium adsorption amount of the CS was measured using the following equation:

$$q_e = \frac{(c_0 - c_e)v}{m} \quad (1)$$

where  $q_e$  (mg/g) is the equilibrium adsorption amount,  $c_0$  (mg/L) the initial concentration of dye solution,  $c_e$  (mg/L) the equilibrium concentration of dye solution,  $v$  (L) the volume of dye solution, and  $m$  (g) the mass of CS.

### 2.3. Characterization

Crystalline phases in samples were identified by powder X-ray diffraction (XRD) analysis using a Philips X'Pert PRO diffractometer (Xpertpro, PHILIPS, Netherlands), and spectra within the range between 10° and 90° ( $2\theta$ ) were recorded at 40 mA and 40 kV using Cu K $\alpha$  radiation ( $\lambda = 0.1542$  nm). The scan rate was 2°/min with a step size of 0.05°. Microstructures and morphologies of the final products were observed by using a field-emission scanning electron microscope (FE-SEM, Nova400NanoSEM, FEI, USA). The density of CS was measured by an automatic actual density analyzer (AccuPyc 1330 Gas Pycnometer, Micrometrics, USA). For each sample, at least 200 carbonaceous spheres from different SEM images were generally measured, and their mean diameter and size distribution were then evaluated. Chemical composition of as-prepared CS was analyzed using an induced coupled plasma emission spectroscope (ICP, Spectro Flame, Spectro Analytical Instrument, Germany). Thermal analysis was carried out in air by using a STA 449F3 Thermal Analysis System (NETZSCH Co., Germany) with a heating rate of 15 °C/min and an air flow rate of 30 mL/min. Nitrogen adsorption/desorption measurements were performed by using a gas sorption analyzer (Autosorb-1-MP/LP, Quantachrome, USA). The samples were out-gassed at 300 °C for 1 h under vacuum in the degas port, and the specific surface area was calculated based on the Brunauer Emmette Teller (BET) model. Surface functional groups were analyzed by using Fourier Transform Infrared Spectroscopy (FTIR, VERTEX 70, Bruker, Germany). The adsorption of MB was examined by Ultraviolet–visible spectroscopy (UV–Vis, UV-2550, Shimadzu Corporation, Japan).

## 3. Results and discussion

### 3.1. Effect of reaction temperature on the preparation of CS

Shown in Fig. 1 are XRD patterns of glucose precursor and as-prepared samples (T1, T2 and T3). As revealed by Fig. 1a, the glucose was of high crystallinity. However, for the prepared CS, a broad diffraction peak appeared at around 24.8° ( $2\theta$ ), indicating that they were amorphous. Moreover, for the sample (T1) car-

**Table 1**  
Batch compositions and processing conditions for CS preparation.

Codes	Reaction temperature/°C	Concentration of glucose/(mol·L <sup>-1</sup> )	Reaction time/h	pH value
T1	160	0.3	12	
T2	180			
T3	200			
C1	180	0.3	12	
C2		0.5		
C3		0.7		
R1			8	
R2	180	0.5	12	
R3			16	
P1				2
P2	180	0.5		3
P3			12	6
P4				9
P5				12
P6				13
P7				14

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