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Synthesis of Carbon Spheres of Controlled Size by Hydrothermal Method

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Abstract

Carbon Spheres were fabricated by hydrothermal method and their structural properties were investigated. Carbon Spheres with average sizes around of 230, 320 and 430 nm were synthesized in different concentration of glucose aqueous solution and different hydrothermal reaction time. The temperature of 180 °C by a hydrothermal reaction was fixed in all of glucose concentration and hydrothermal reaction time. The result showed that the spherical shape of Carbon Spheres was formed in the special concentration of glucose aqueous solution and hydrothermal reaction time.The product obtained was characterized by X-ray diffraction(XRD); Fourier transforms infrared (FTIR) spectra, which have inferred the Carbonic nature of the product. Further,SEM images have revealed the spheres having quite spherical morphology.

1. Introduction

Carbonic materialsareone of the most important functional materials due totheir unique electromagnetic, thermo dynamical and mechanical properties [1]. These materials exhibit potential applications in many areas such as drug delivery, hydrogen storage, junction devices, and sensors[2, 3]. Many trials have been made for the synthesis of nanoparticles with controllable structure and size. Spherical nanoparticles are very commonly generated due to the minimum surface energy compared to other structures (e.g., films, tubes, rods)[4]. Recently, Carbon Spheres (CSs) have attracted a great interest owning to their unique properties, their potential applications including high-density and high-strength carbon artifacts lithium storing materials [5-8], sacrificial template to prepare hollow structures(e.g., TiO_2 hollow spheres) [9-16], catalyst support material in methanol electro-oxidation [17], good mechanical stability, chemical inertness, porous nature with large pore volume, and coating material in core/shell structure [7,18, and 19]. An important insight gained by the discovery of carbon nanostructures is that the carbon atoms can form pentagonal and heptagonal carbon rings, and the combination of these two basic structural units with the hexagonal carbon rings can form a variety of morphologies.

The functional properties of nanoparticles are heavily dependent on their shapes, sizes, and size distribution. Various methods can be used to fabricate of carbon spheres, such as chemical vapor deposition [21], arc plasma technique, templating method [22], pyrolysis carbon sources [23], and hydrothermal method. Some of the methods require complicated equipment and strict experimental condition. Among them, the hydrothermal method is widely used for synthesis of carbonic materials [24]. In this method the closed system, characterized by low temperature growth and a suitable atmosphere to produce oxidizing or reducing conditions is an excellent approach to produce carbon polymorphs. Thus, hydrothermal technique allows the synthesis of phases, which cannot be stabilized by any other method at such low pressure-temperatures. This general approach provides an efficient, scalable route to synthesize spherical, porous carbon particles with porous structure and is suitable for large scale manufacturing. Moreover, the Carbon Spheres produced by the hydrothermal approach have a hydrophilic surface covered with C–OH groups, which are available for further surface functional modification, as well as the Carbon Spheres can be easily removed by oxidation at high temperature or by dissolving via enzyme in solution. Nowadays, mesoporous carbon particles with rod, fiber, plate, and donut-like morphologies were prepared by using mesoporous silica templates. Therefore, many studies focused on the synthesis of carbon spheres via the hydrothermal approach.

Despite some successes, limitations still exist in generating monodispersed Carbon Spheres. This is because it is difficult to control or adjust the concentration of the precursor in a sealed system, which will affect the nucleation and growth, and hence the morphology and size of Carbon Spheres. Therefore, to develop a simple and efficient method to prepare monodispersed Carbon Spheres is still challenging [1, 22, and 25].

In this research, we report the synthesis of Carbon Spheres of controlled size by a hydrothermal method. The average size of Carbon Spheres was around230, 320 and 430 nm for different glucose concentration and different hydrothermal reaction time. The glucose concentration was selected as 0.5 M, 1.0 M and 1.5 M. The hydrothermal reaction time wasseton 3 h, 8 h and 16 h. However, the spherical structures were found for special glucose concentration and hydrothermal reaction time. The particle characteristics (shape, size, distribution) are then characterized by using various techniques, including scanning electron microscopy (SEM),FTIR spectrum analysis, and X-ray diffraction.

2. Experimental procedure

2.1. Synthesis of Carbon Spheres

Carbon spheres with different sizes were synthesized by a hydrothermal method. Briefly 25 ml of an aqueous solution of glucose with different concentrations of 0.5 M, 1 M and 1.5 M was prepared. Then it was transferred to a 100 ml Teflon-lined stainless steel autoclave and sealed and maintained at 180 ºC for 3 h, 8 h and 16 h. The dark brown precipitate was centrifuged at 2000 rpm for 10 min and washed with ethanol and DI water for four times. Finally the carbon spheres were dried at 70 ºC for 4 h.

2.2. Characterization

The morphology and size of the Carbon Spheres were checked using scanning electron microscope (T-Scan System). To prepare the SEM sample, a drop of the diluted suspension was placed on a glass slide and then it was coated with gold prior to examination. The average particle size was estimated based on the SEM image. FTIR spectrum (Perkin Elmer, Spectrum one NTS) was used to identify the functional groups. The X-ray diffraction pattern was also recorded with Cu Kα radiation by a Philips Xpert-pro system.

3. Results and discussion

Carbon Spheres with different sizes synthesized by hydrothermal method in different concentration of glucose aqueous solution and hydrothermal reaction times. The fine and spherical shape of them formed in special concentration of glucose aqueous solution and hydrothermal reaction times.Fig. 1 demonstrated the SEM images of the Carbon Spheres prepared at 0.5 M concentration of the glucose aqueous solution and with the hydrothermal time 8 h. It could be seen that the average size of Carbon Spheres is about 230 nm. The size distribution histogram of the Carbon

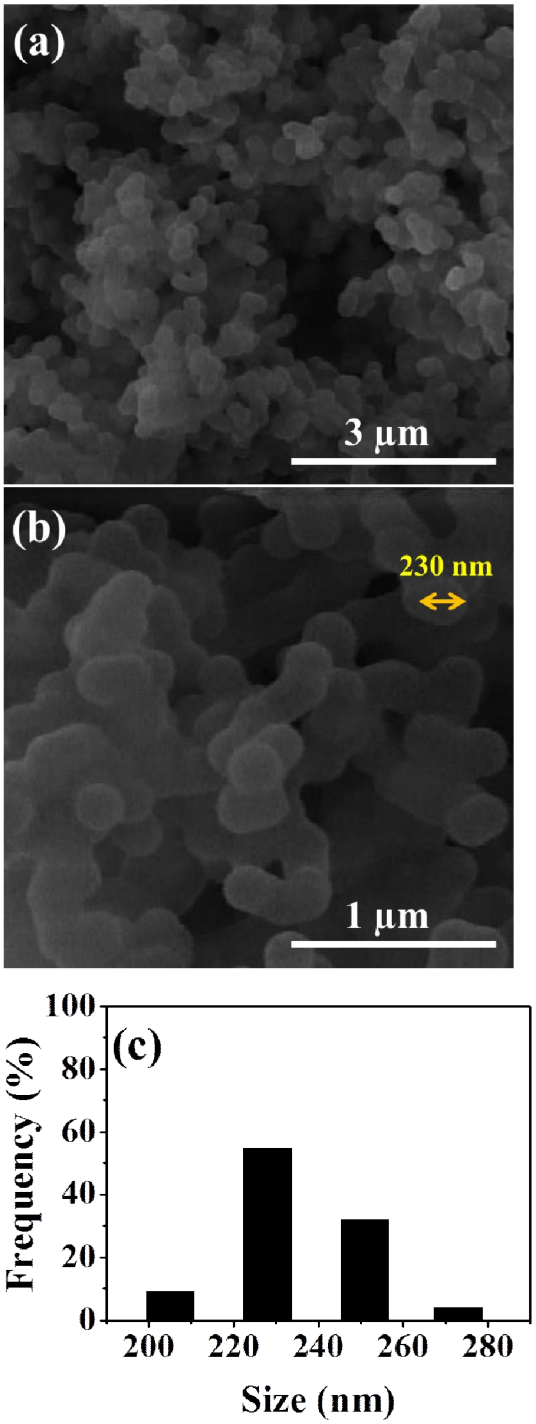

Fig.1.SEM images of Carbon Spheres prepared with glucose concentration of 0.5 M in 3 µm scale (a), 1 µm scale (b) and histogram of size of them (c).

Spheres is shown in the Fig. 1c too.

In the hydrothermal time 3 h, these structures didn't form, because at this time the powder of Carbon Spheres has not received. By increasing the glucose concentration to 1 M and 1.5 M, the power of Carbon Spheres didn't preserved. So this time isn't good for hydrothermal reaction in all of glucose concentrations and this time was omitted. In the hydrothermal time 16 h, these structures didn't form, because at this time the product of autoclave were burnt especially in 1.5 M glucose concentration. So this time was so long for hydrothermal reaction in all of glucose concentrations and this time was omitted too.

Fig. 2 demonstrated the SEM images of the CarbonSpheres prepared at 1 M concentration of the glucose aqueous solution and with the hydrothermal time 8 h. According to size distribution of them (Fig. 2c), it could be seen that the most of Carbon Spheres size is around 320 nm. In this case, when the glucose concentration increased the average size of these spherical structures was increased.

The morphology and structure of the samples were also investigated by SEM images. The Carbon Spheres have been prepared in 1.5 M glucose concentration, shown in Fig. 3. In these images, the spherical Carbon structures are quit spherical with 435 nm diameter. Also the size distribution histogram of the Carbon Spheres is shown in the Fig. 3c. According to it, the most of the Carbon Spheres diameter is approximately 435 nm.

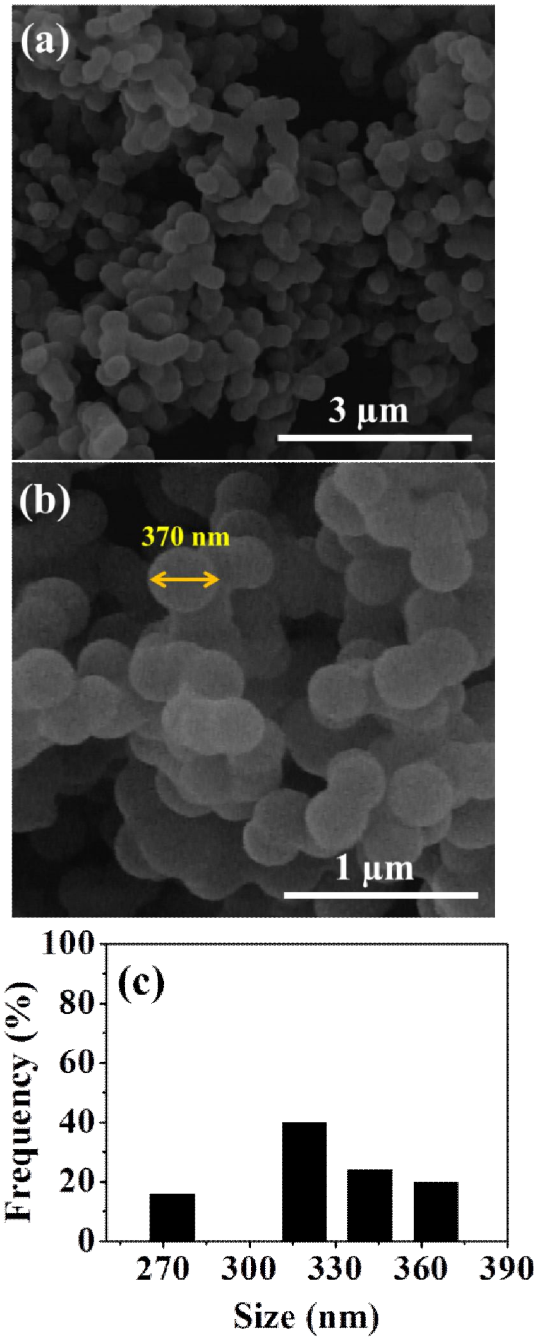

Fig.2.SEM images of Carbon Spheres prepared with glucose concentration of 1 M in 3 µm scale (a), 1 µm scale (b) and histogram of size of them (c).

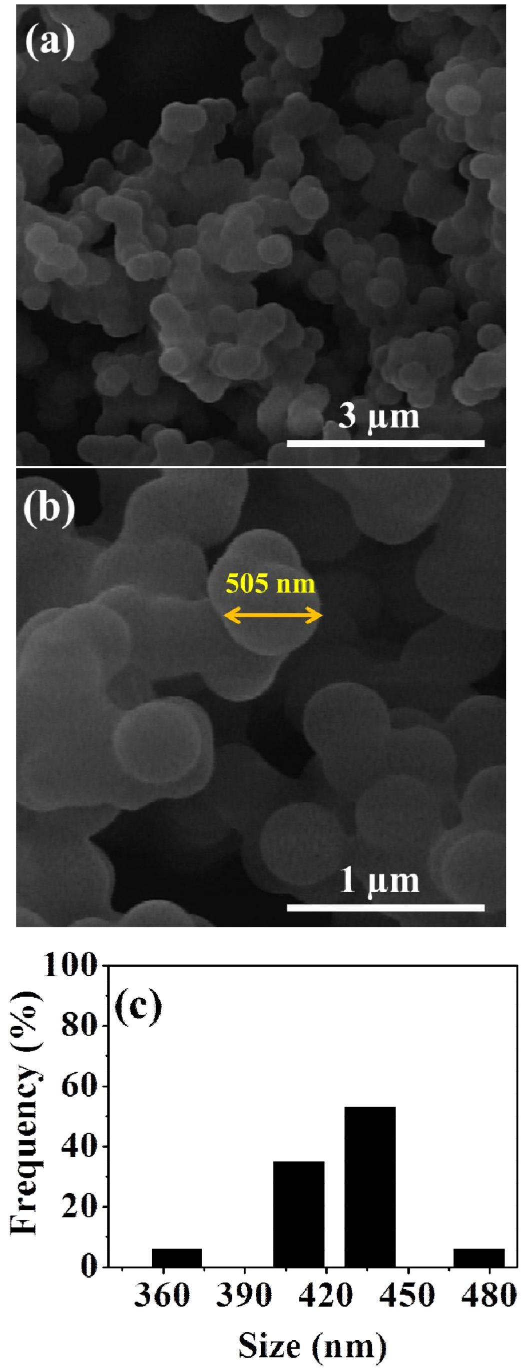

Fig.3.SEM images of Carbon Spheres prepared with glucose concentration of 1.5 M in 3 µm scale (a), 1 µm scale (b) and histogram of size of them (c).

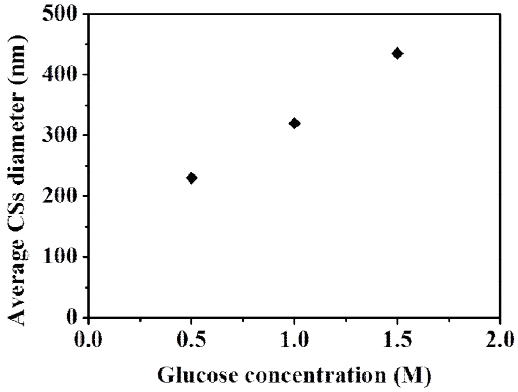

Fig.4. Effect of glucose concentration to diameter of Carbon Spheres.

When the glucose concentration was increased, the diameter of resulting Carbon spheres was increased. In addition, a graph of the average diameter of Carbon Spheres and the glucose concentration aqueous solution were liner (Fig. 4). Therefore, the diameter of the carbon sphere can be easily controlled by adjusting the concentration of the glucose solution.

There are numerous works on the chemical transformations that take place when glucose is treated under pressure in sub- or supercritical water in the literature [26]. From this information it is possible to reconstruct the mechanism of the formation of hydrochar products from glucose. This is schematically illustrated in Fig. 5. The final product of this hydrothermal approach is the Carbon Spheres with hydrophobic core and hydrophilic sell. This schematic is showing in Fig. 5.This is so useful for using of Carbon Spheres as template because hydrophilic shell cause to easy dispersion of them to ethanol and water. Then thissolution makes a good place for two dimension growth of nano structures on the surface of them.

We also used the X-ray diffraction (XRD) to examine the phase of Carbon Spheres and found that the sample is amorphous (Fig. 6). Two peaks at around 24 ° and 43°2Θ can be seen for Carbon

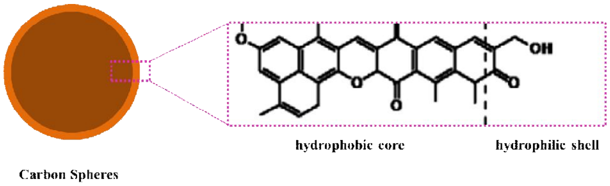

Fig.5. A schematic of Carbon Spheres prepared with glucose.

Spheres with around 320 nm diameters. These two broad peaks are assigned to (002) and (101) planes of carbon materials.

The chemical transformations that occur when the glucose is converted into carbonaceous products by means of hydrothermal carbonization.An FTIR spectrum of Carbon spheres with around 320 nm diameter is shown in Fig. 7. It can be seen that the FTIR spectra of the sample contain several bands which reveal that aromatization processes take place during hydrothermal carbonization. The presence of aromatic rings is also evidenced by the band at 1620 cm^{-1}, attributed to C=C vibrations [27,32], and to the bands in the 875–750 cm^{-1} region, assigned to aromatic C-H out-of-plane bending vibrations [36]. These hydrochar materials also possess aliphatic structures, as can be deduced from the band at 3000–2815 cm^{-1}, which corresponds to stretching vibrations of aliphatic C-H [37,38]. Moreover, the presence of oxygen groups is suggested by the bands at: 3000–3700 cm^{-1} (a wide band attributed to O-H stretching vibrations in hydroxyl or carboxyl groups) [37], 1710 cm^{-1} (C=O vibrations corresponding to carbonyl, Quinone, ester or carboxyl) [35] and 1000–1460 cm^{-1} (C-O stretching vibrations in hydroxyl, ester or ether and O-H bending vibrations) [35]. The decrease (in relation to raw cellulose) in the intensity of the bands at 1000–1460 cm^{-1} and the broad band at 3000–3700 cm^{-1} suggest that dehydration occurred during the hydrothermal carbonization of the glucose.

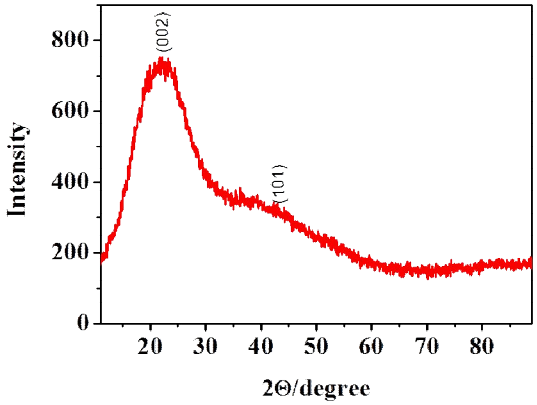

Fig.6. TheX-ray diffraction pattern (XRD) of the Carbon Spheres with around 320 nm diameter.

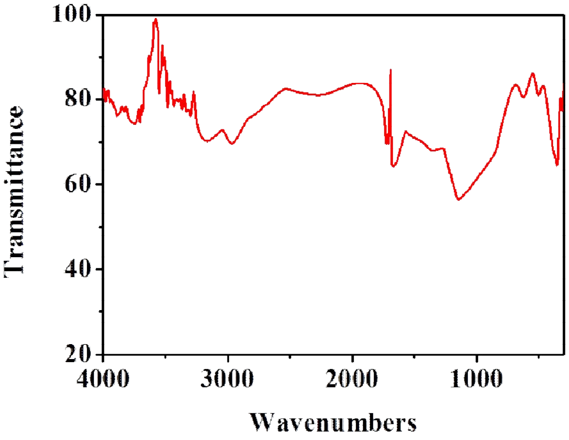

Fig.7. TheFT-IRspectrum of the Carbon Spheres with around 320 nm diameter.

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