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Investigation of hydrothermal process time on the size of carbon micro- and nano-spheres

Khadijeh Hemmati[1], Esmaiel Saievar-Iranizad [*,1], Amir Bayat[1]

[1]Department of Physics, Faculty of Basic Science, Tarbiat Modares University, Tehran, Iran.

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Abstract: In this study, carbon nano-micro spheres with tightly controllable size, regular and perfect shape, high yields and narrow size distribution were prepared simply from glucose and DI water as precursors using a hydrothermal method. By setting the initial concentration of glucose solution and changing the hydrothermal process time at a constant temperature of 160 °C, carbon spheres with various sizes were synthesized in a sealed autoclave. The relationship between the average carbon sphere size and hydrothermal process time has been discussed. By increasing the hydrothermal process time at a constant temperature (160 ° C) and a constant concentration of glucose solution (0.75 molar), carbon nano-micro spheres were obtained. The diameters of carbon nano-micro spheres synthesized in this study ranged from 90 nm to 4.5 µm. The obtained carbon nano-micro spheres were analyzed by different techniques including scanning electron microscopy (SEM), X-ray diffraction patterns (XRD), energy dispersive spectrometry (EDS) and Raman analysis. In addition, the existence of surface functional groups on carbon nano/micro spheres was characterized by Fourier transform infrared (FTIR) measurements.

Keywords: Carbon microspheres, Carbon nanospheres, Hydrothermal process

1. INTRODUCTION

Due to the intrinsic and excellent properties of carbon materials such as high thermal resistance, high strength, controllable structure, electronic properties and excellent chemical stability, various structures of this material including nanotubes, nanorods, fullerene and recently carbon micro and nano spheres has been used more and more frequently in several industrial and academic applications [1-6]. In recent years, carbon nano-micro spheres have attracted lots of attention due to their wide range of applications such as hydrogen storage systems, electrode for supercapacitors, anode in secondary lithium batteries,

[*]**Corresponding author. E-mail: saievare@modares.ac.ir**

templates for hollow structures, semiconductor nanoparticles and as anode catalyst support for direct methanol fuel cells [7-12]. Therefore, for preparation of the carbon nano-micro spheres many methods such as chemical vapor deposition [13], hydrothermal [2, 6, 14], solvothermal [15], chemical routs and ultrasonic have been proposed by many researchers. Unfortunately, all these methods are not useful for large application. In this research, simple and large scale hydrothermal method by adjusting some parameters including initial concentration of glucose, annealing time and temperature were used for the production of carbon nano-micro spheres.

2. EXPERIMANTAL SECTION

Materials and characterization:

The morphology and composition of prepared samples were investigated by scanning electron microscope (SEM) Phenom ProX Model equipped with an energy dispersive spectroscopy (EDS). In order to study the crystal structure, the powder X-ray diffraction (XRD) patterns were recorded on a X'Pert MPD X-ray diffractometer with Co Kα (= 1.78897 A˚) radiation at 40 kV and 40 mA. The surface functional groups of the samples and type of their bonds were analyzed by Fourier transform infrared spectroscopy (FTIR) on a Shimadzo 4300 spectrophotometer by using a standard disk technique of samples mixed with KBr in a 1:100 ratio. Raman scattering measurements of the samples were performed on an Almega Thermo Nicolet Confocal Laser MicroRaman spectrometer using an Nd/ YLF laser with 532 nm Radiation. Chemical solutions were prepared using glucose purchased from Merck Co (Germany) and for washing the product, absolute ethanol (99.95 %) were purchased from Merck Co (Germany).

Chemical process:

In this experiment, in order to synthesis carbon nano-micro spheres, an amount of glucose was dissolved in di-ionized (DI) water to create glucose solutions with concentration of 0.75mol/lit. The resulting solutions were transferred into a 75 ml cylindrical Teflon located in a stainless steel autoclave and put into an electric furnace. The furnace was adjusted by the way that at the beginning it reached from the room temperature to the desired temperature of 160 ˚C within 1 hour, and stayed in this temperature at given times of 8, 10, 16, 23 and 32 hours (named as a, b, c, d and e, respectively) and then it reached to the room temperature naturally. After hydrothermal process, in order to collect and wash the obtained product, the solutions (brown or black in color) were centrifuged at 9000 rpm. After three times washing the precipitates with deionized water and absolute ethanol, the products dried at 80° C for 5 hours in an oven.

3. RESULTS AND DISCUSSION

SEM analysis was used for determination the morphology and diameter of the obtained nano-micro spheres as shown in Figure 1. According to this Figure, the carbon nano-micro spheres are synthesized properly in sphere shape and the effect of hydrothermal process time on the diameter of spheres is obvious. Increasing hydrothermal process time leads to an increase in diameter of carbon nano-micro spheres because more molecules can reach the central core, and as a result, bigger spheres can be produced. The relationship between the average carbon sphere size and hydrothermal process time is shown in Figure 2. As seen, the carbon sphere size increases as hydrothermal process time is increased.

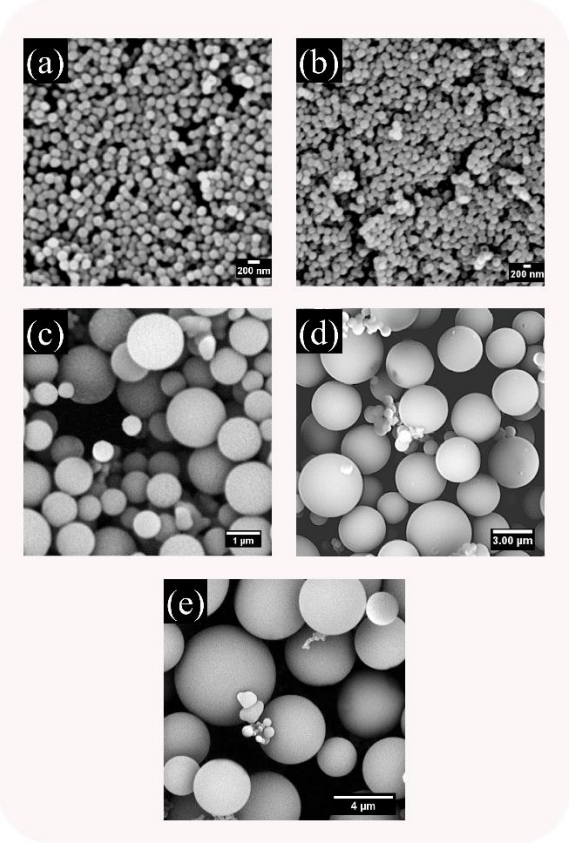

Fig. 1. SEM images of carbon nano-micro spheres

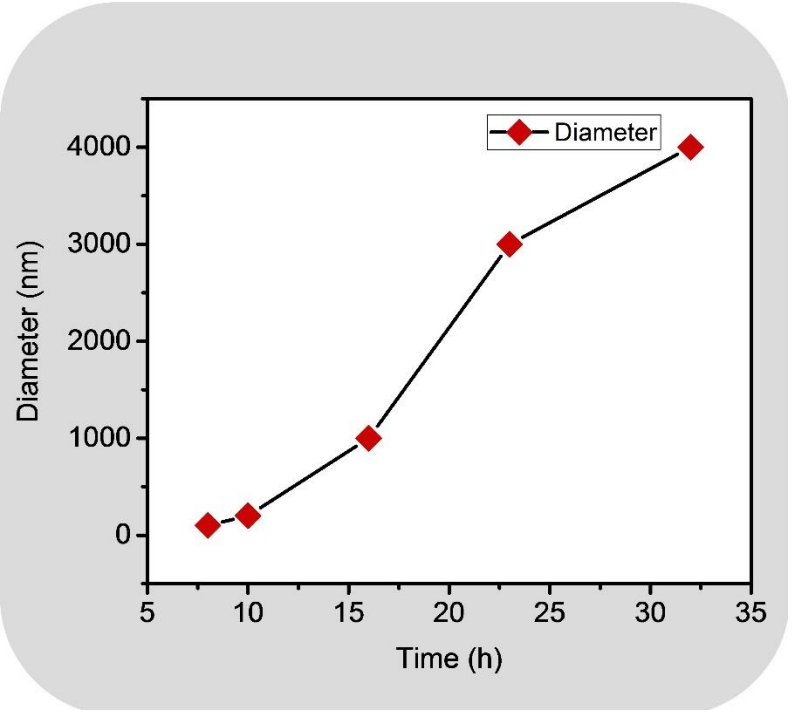

Fig. 2. The relationship between the average carbon sphere size and hydrothermal process time.

XRD patterns of the obtained carbon spheres (0.75 mol/lit) at 160˚C for 23 h is shown in Figure 3. As it can be seen, there is two peaks at 2θ=24 ˚ and 43 ˚, which originate from (002) and (101) planes of graphitic structure, respectively. Existence of these two peaks shows that crystallinity of the samples is low and the spheres are in amorphous phase.

Figure 4 shows energy dispersive spectroscopy (EDS) spectrum of the samples. According to this Figure, the spheres are produced with carbon and oxygen and amount of carbon is higher than that of oxygen. Oxygen peak can be originated due to incomplete decomposition of glucose, existence of carboxyl and hydroxyl functional groups, or adsorption of water on the carbon sphere surfaces.

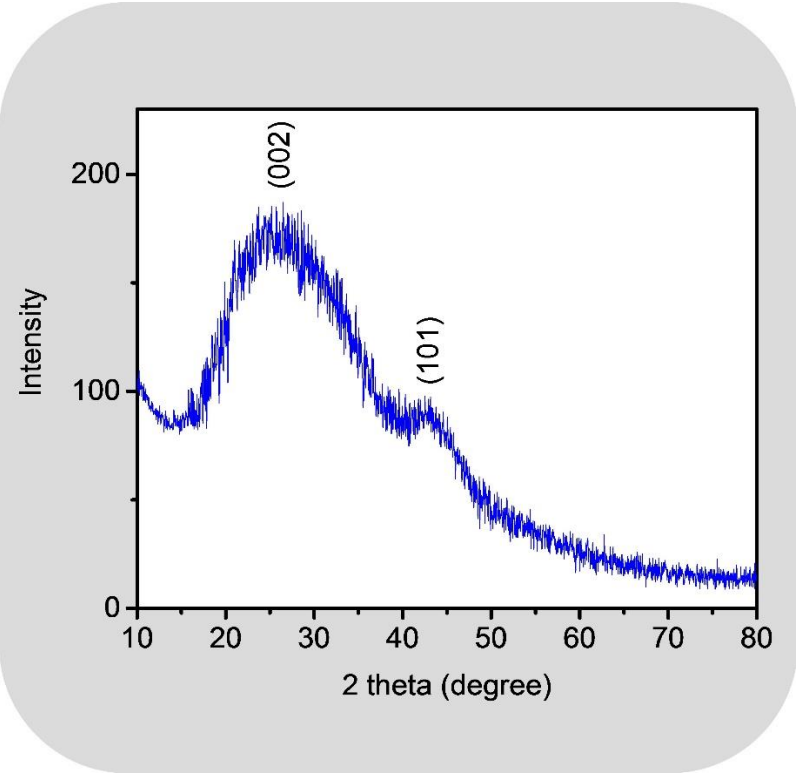

Fig. 3. XRD pattern of the obtained carbon spheres (0.75mol/lit) at 160˚C for 23 h.

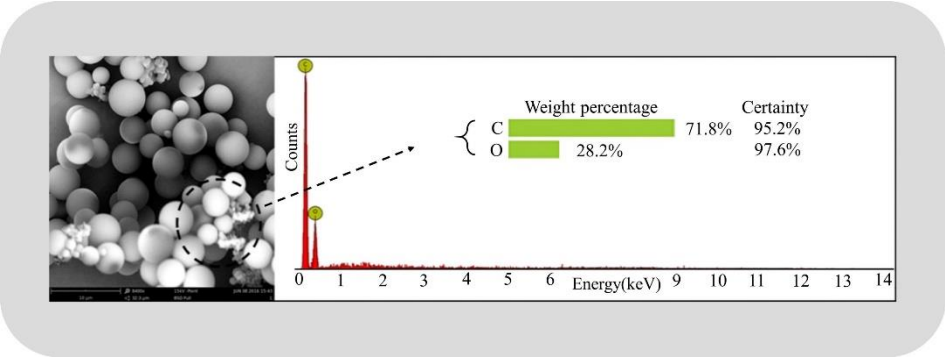

Fig. 4. SEM micrographs and energy dispersive spectroscopy (EDS) of the obtained carbon spheres (0.75mol/lit) at 160˚C for 23 h.

The experimental conditions and the diameter of the carbon nano-micro spheres obtained are given in Table 1.

Table 1. Experimental parameters of the obtained carbon nano-micro spheres at 160˚ C.

Sample no	Solution concentration (mol/lit)	Hydrothermal time (h)	Hydrothermal temperature (°C)	Diameter size (nm)
a	0.75	8	160	90-110
b	0.75	10	160	190-210
c	0.75	16	160	800-1200
d	0.75	23	160	2500-3500
e	0.75	32	160	3500-4500

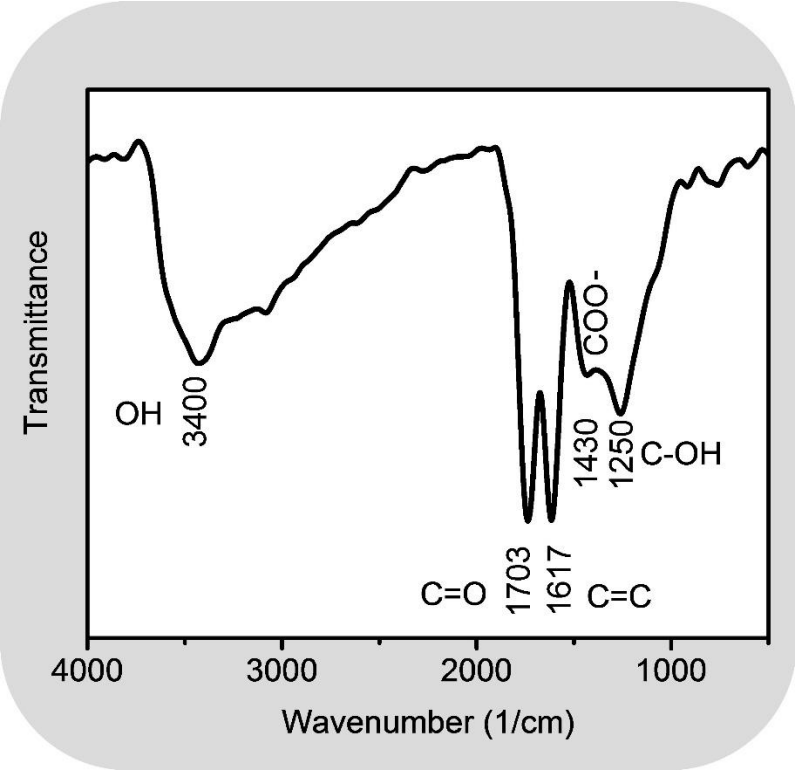

Fig. 5. FT-IR spectra of obtained carbon spheres (0.75mol/lit) at 160˚C for 23 h.

Surface functional groups along with surface are known to play an important role in many properties and applications of carbon nano-micro spheres as catalysts and templates [6] in addition to biochemistry, diagnostics, and drug delivery [16]. As depicted in Figure 5, the infrared spectrum of carbon nano-micro spheres showed functional groups which are mainly attributed to hydroxyl and carboxyl

groups. Hydroxyl groups include peaks in the range of 3200–3500 1/cm attributed to O-H stretching vibration and 1250 1/cm to C-OH stretching and OH bending vibrations in C-OH, respectively. Carboxyl groups include peaks at 1617 1/cm ascribed to C=C stretching vibrations, 1703 1/cm ascribed to the stretching vibration of C=O and 1430 1/cm attributed to the symmetric stretching vibration of carboxylic group -COO- [6, 11, 16]. The spectrum of the carbon spheres indicated that –OH (hydroxyl groups) was the primary functional group.

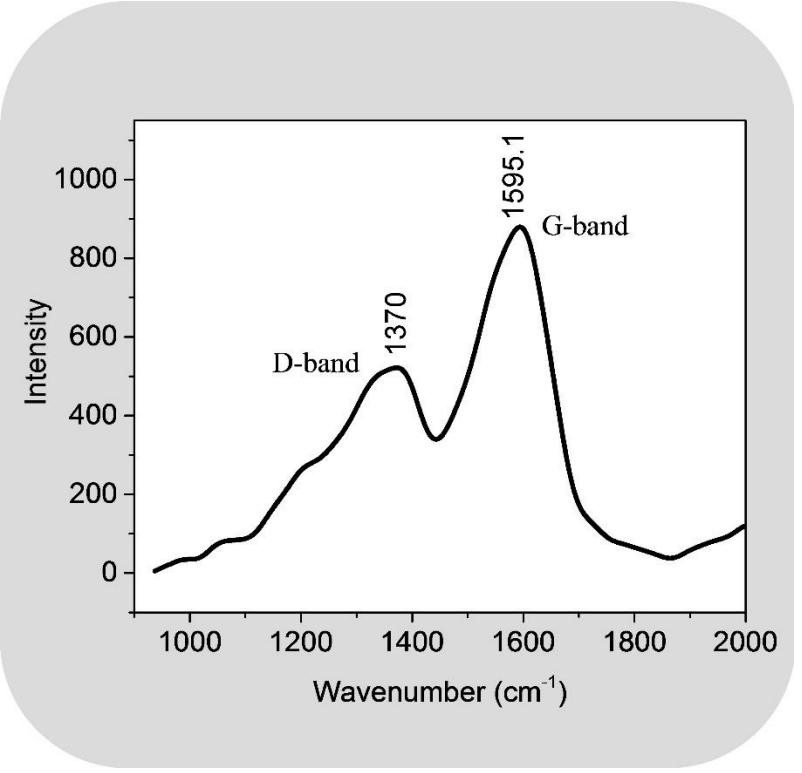

Fig. 6. Raman spectrum of the obtained spheres (0.75mol/lit) at 160˚C for 23 h.

Raman spectroscopy is a versatile technique for studying the properties of carbon materials. In Figure 6 the Raman spectra of the obtained carbon spheres (0.75 mol/lit) at 160˚ for 23 h is shown. The Raman spectrum of carbon spheres consists of two distinct bands (Fig. 6), usually named as G band and D band. The strong G band peaked at "1595 "1/cm and corresponds to an E2g mode with high-frequency of graphite layer at Γ point. The D band at "1370" 1/cm is a breathing mode which is related to the vibrations of carbon atoms in plane ending of disordered graphite near K zone boundary. The wideness of D band is associated to the defects and disorders in structure of synthesized samples [2, 14]. The I(D)

/I(G) ratio can be used as a measure of graphitization degree of carbon materials. For the carbon spheres synthesized in this study, the value of I(D) /I(G) is 0.59, which implies that the graphitization degree is low, and this conclusion is in agreement with the XRD analysis shown in Fig 3, where confirms the existence of only two peaks of graphite structure and broadening of them.

4. CONCLUSION

In summary, we synthesized carbon nano-micro spheres using a simple and large scale method with controllable diameter size in different conditions. XRD pattern and EDS analysis showed the graphitic nature of carbon spheres and SEM images proved that diameter of carbon nano-micro spheres depends on the concentration of glucose. Also FTIR measurements confirmed the presence of functional groups. The Raman spectrum of the obtained carbon spheres indicated the formation of amorphous carbon structure. This very simple and inexpensive method for synthesis of carbon nano-microspheres can be used for different large applications.

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