



Synthesis of uniform and size-controllable carbon nanospheres by a simple hydrothermal method and fabrication of carbon nanosphere super-hydrophobic surface



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ABSTRACT

A simple hydrothermal method was used to produce high yield, monodisperse and tightly controllable size of carbon nanospheres (CNSs) by adjusting the concentration of initial sucrose solution in a sealed autoclave at 170 °C for 8 h. By changing the solution concentration from 0.5 to 0.1 mol l⁻¹, the sizes of carbon spheres (CS) were reduced from about 2500 to about 300 nm. Also by increasing the solution volume to the vessel volume ratio (V_s/V_v) from 5/6 to 11/13, the yield of CS was increased from 25% up to about 55% of initial raw materials. It was found that by post-annealing of the 300 nm CNSs at 435 °C for 30 min, their diameters were reduced to 100 nm. Moreover, annealing in air atmosphere had a noticeable influence on the surface functional groups and bonds of CNSs. In addition, CNSs were used to fabricate hydrophobic surfaces by coating their ethanolic colloidal solution on glass substrates. The measured contact angle (CA) of a water droplet was about 153°, indicating that the CNSs thick layers were super-hydrophobic. The size dependence of CNSs on the different parameters has been discussed.

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1. Introduction

After discovery of carbon nanotubes and fullerenes, an intense interest in the application of different carbon nanostructures was motivated. Recently, carbon nano- and microspheres have attracted great attention due to their wide range applications such as electrode for supercapacitors, anode in secondary lithium batteries, material reinforcement, templates for hollow structures, capsules for magnetic nanoparticles, refinement of aqueous solutions, catalyst for direct methanol fuel cells, etc. [1–6].

It is obvious that the improvement of these applications strongly depends on the ability of controlling the size and surface properties of carbon spheres (CS). Many methods have been developed to synthesize the CS consisted of chemical vapor deposition [7], pyrolysis [8], hydrothermal [9], solvothermal [10] and chemical routes [11]. Each method has its own advantages and disadvantages. In one hand, needing special precursors, apparatus, and high temperature synthesis and in the other hand, producing toxic compounds and very low yield products are some of the problems which occur in CNSs production. High yield production (>95%), high purity (>99%), narrow size distribution and having sizes in the nanoscale range

are desired parameters in CNSs production. Only a few methods produce CS with some of these favorites, simultaneously [5,12,13]. Based on a recent “green” simple hydrothermal method [14], a procedure was employed in which by tuning some parameters offers a good way to precise control of the CS size and leads to a high yield and high purity of products. Also, a simple thermal treatment is presented for further reduction of CS diameters down to the nanoscale range. To the best of our knowledge there is no any other report on precise control of CS size by adjusting only the initial solution concentration or applying a thermal treatment on as-prepared CSs.

Hydrophobicity is one of the interesting properties of the solid surfaces that depends on the topography and chemistry of the surface. Based on the two main models proposed by Wenzel and by Cassie and Baxter, existence of micro- and nano-scale cavities and roughness are essential in order to have hydrophobic surfaces [15,20]. Artificial super-hydrophobicity with contact angle (CA) bigger than 150° can be achieved by making rough topography on a surface with or without a covering material that reduces free energy of the surface [15]. Moreover, it is commonly believed that super-hydrophobicity is a result of the presence of combined binary geometric structures at the micro- and nanometer scales [18,19]. In this regard, many methods like electrochemical deposition and chemical etching have been developed to fabricate super-hydrophobic surfaces, but due to their limitations such as severe conditions and expensive materials, developing simple and cheap techniques is required [16].

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Because of polymeric structure and spherical shape, CNSs are inherently hydrophobic [20] and can settle into a regular arrangement when forming surface coatings. So the formation of super-hydrophobic surfaces using these entities can be expectable. Recently, Qu et al. [19] reported a method for preparing super-hydrophobic surfaces by using carbon nanosphere films that were made by depositing the soot of burning rapeseed oil. Although the method was extremely cheap, facile and time-saving, however, they had no control over the size of fabricated CNSs and being unsuitable for using in bulk conditions. On the other hand, it seems that size controllable CNSs in powder form, synthesized by our developed route may have more applications. So, as an application, a thick layer of CNSs was coated on a glass substrate by spin coating technique and exhibited a good super-hydrophobicity. Accordingly, and by considering the non-toxicity, insulating and anti-corrosive nature of CNSs these materials can be considered as promising materials for fabricating the super-non-wettable surfaces having great potential in industrial applications.

2. Experimental

2.1. Sample preparations

In a typical procedure, proper amounts of sucrose (Analytical Grade, Merck Chemical Reagents Company, Germany) were dissolved in DI water to prepare sucrose solutions with five different concentrations of 0.1, 0.2, 0.3, 0.4 and 0.5 mol l⁻¹. The solution was then transferred into a 160 ml Teflon lined stainless steel autoclave. The autoclave was sealed and put into an electric furnace. The furnace temperature was increased from room temperature to 170 °C in 40 min and kept at 170 °C for 8 h. The autoclave was then allowed to cool down to room temperature naturally. The dark products were collected by using a 4000 rpm centrifuge and washed several times with DI water and absolute ethanol then dried at 60 °C for 10 h. We found that the optimum reaction temperature and time of 170 °C and 8 h were critical in production of high yield and high pure of CS. For shorter times and lower temperatures, the amount of deduced products was lesser while longer times and higher temperatures led to production of CSs with sizes bigger than that of the optimum conditions. The different prepared batches were named as CS(*j*) (*j*=0.1, 0.2, 0.3, 0.4 and 0.5) where *j* is the concentration of initial sucrose solution. The solution volume to the Teflon vessel volume (V_s/V_v) in our experiments was chosen 5/6 for different samples. But it was found that by increasing the V_s/V_v ratio from 5/6 to 11/13 the amount of final product was increased from 25 to about 55% of initial raw materials. We believed that these ratios were optimum to adjust true and enough vapor pressure in the Teflon vessel during the reaction process and led to CS with minimum size and maximum yield. At higher ratios, the Teflon vessel was seriously damaged. In fact the vapor pressure of the solution is an effective factor in formation of nanoparticles in a sealed autoclave.

Thermogravimetric analysis (TGA) was performed to examine thermal stability of prepared CNSs and to determine their decomposition temperature. A post-annealing treatment was also performed in order to investigate the effect of heating on the morphology and possible size reduction of CNSs. Four parts of CS(0.1) samples in powder form were put into alumina boats, annealed at different temperatures for various times. The first part was annealed at 395 °C for 30 min and the other three parts were annealed at 435 °C for 15, 30 and 40 min. The heating rate was chosen 10 °C/min except for the sample which was annealed at 435 °C for 40 min which was put into a preheated furnace. It is to be noticed that these times and temperatures were chosen based on TGA data.

For Fourier transform infrared (FTIR) measurements, equal amounts of prepared samples were mixed with KBr in a 1:50 ratio

and dried at 70 °C for 2 h before any measurements to remove possible residual amount of moisture in powders and then pressed into thin pellets.

2.2. Samples characterization

Crystalline structure and phase purity of products were investigated by X-ray powder diffraction (XRD) using an X-ray diffractometer (Phillips, PW-1840, Cu K α (λ = 1.5406 Å) radiation). TGA of the as-synthesized CNSs was carried out by using a thermogravimetric analyzer (BAHR Thermo Analyzer STA 503, Germany) from 40 to 800 °C with a heating rate of 10 °C/min under dry air atmosphere. Scanning electron microscopy (SEM) imaging was performed to observe the morphology and estimate the size of both as-synthesized and treated CNSs by using a scanning electron microscope (SEM; Leo 1455 VP, Germany). FTIR spectra of the samples were recorded on a (BOMEM MB-102, Canada) spectrophotometer to study the type and amount of the surface functional groups and bonds of CNSs.

2.3. Fabrication of hydrophobic surfaces and measurements

In order to fabricate uniform and stable thick film layers of CNSs, glass substrates were firstly kept in a solution of water and 3-aminopropyltriethoxysilane (APTS) with a ratio of 1:50 for 1 day to improve adhesion between functionalized carbon particles and glass surface [17]. Thick film of CNSs were produced by spin coating of colloidal solution of CS(0.4) samples in ethanol on a glass substrates. The speed of spin coater was selected 2400 rpm. Our preliminary experiments showed that under such a condition more uniform CNSs films can be formed on the glass substrates. The as prepared layers were annealed at 200 °C for 5 h in order to remove all hydrocarbon contaminations. It is to be noticed that although the other samples showed hydrophobicity but this size of CNSs showed super-hydrophobicity. Topography and morphology of the CNSs layers were examined by means of AFM and SEM. A power shot G9 Canon camera was used for recording images of water droplet and its motion on empty and coated surfaces in order to calculate the contact angle (CA) and sliding angle of water droplet.

3. Results and discussion

3.1. Samples measurements

Fig. 1 shows the XRD pattern of the as-synthesized CNSs. Two peaks at about 24–25° and 43.1° can be indexed as typical graphitic (002) and (100) planes. But existence of only these two peaks of graphite structure and broadening of them imply that graphitization degree is low. The interlayer distance d_{002} calculated from XRD data is about 3.558 Å that is bigger than that assigned to the ideal graphite structure, namely 3.354 Å indicating considerable disordered carbon structures.

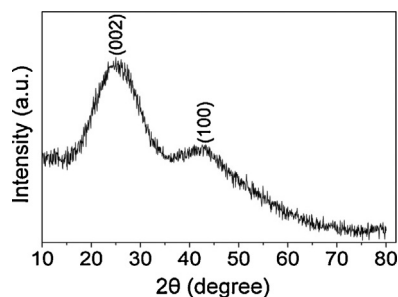


Fig. 1. XRD pattern of as-synthesized CNSs.

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