Hydrothermal Synthesis of Carbon Microspheres from Glucose: Tuning Sphere Size by Adding Oxalic Acid

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Carbon spheres were successfully prepared via hydrothermal treatment of glucose, and spherical size (0.5–8 µm) could be tuned by adding different amount of oxalic acid. The surface of obtained carbon spheres contains hydrophilic functionalities including –OH, –C=O, and COOH groups, which were not destroyed by oxalic acid. This study provided a facile, simple route for producing size-tunable carbon microspheres with functional groups.

Since the discovery of C_{60} fullerene and carbon nanotubes, research on the synthesis and properties of new carbon materials has received considerable attention. Among these, carbon spheres are becoming increasingly important for both academic and industrial fields. Due to intrinsic properties such as high strength, high thermal resistance, and light weight, carbon spheres have been widely used as high strength composites, catalyst supports, lubricants, gas storage media, and electrode materials for lithium-ion batteries, especially as "green" template materials for the preparation of hollow materials with spherical structure.[1]

Until now, many attempts have been made toward the synthesis of carbon spheres, such as chemical vapor deposition (CVD),[2] arc discharge,[3] thermal treatment of carbonaceous materials,[4] and reduction of supercritical CO_2.[5] However, complex equipment and rigorous conditions restricted further application as general methods. In comparison, hydrothermal synthesis of carbon spheres appears to be an easy route, and recently it has been reported that carbon spheres could be synthesized readily by hydrothermal treatment of sugars like glucose.[6] However, hydrothermal methods give relatively smaller tunable diameters. This disadvantage restricts the further application of carbon spheres because different sizes determines different properties. Thus, there is an urgent need for cost-effective production of size-tunable carbon spheres by using hydrothermal methods.

In this paper, we introduce an improved method to prepare carbon spheres using hydrothermal treatment of glucose. The key point of this approach is the size of carbon spheres could be tuned by manipulating the amount of added oxalic acid. Furthermore, the hydrophilic surface of carbon spheres is retained during treatment by oxalic acid.

All reagents in this work were of analytical purity and used without further purification. In this experiment, 4 g of glucose and a certain amount of oxalic acid were dissolved in 40 mL of deionized water to form a clear solution and then poured into a 50-mL capacity Teflon-lined stainless autoclave. The molar ratio of oxalic acid to glucose (R) varied from 0/4 to 0.5/4. The autoclave was maintained at 180 °C for 12 h and then air-cooled to room temperature. The resulting products (1.2 g) were obtained by isolating with centrifugation, cleaning by three cycles of centrifugation/washing/redispersion in water and in alcohol, and oven-dried at 80 °C for more than 4 h. The yields of products obtained at $R = 0/4$, 0.125/4, 0.25/4, and 0.5/4 are 81.15, 66.67, 76.68, and 77.72%, respectively.

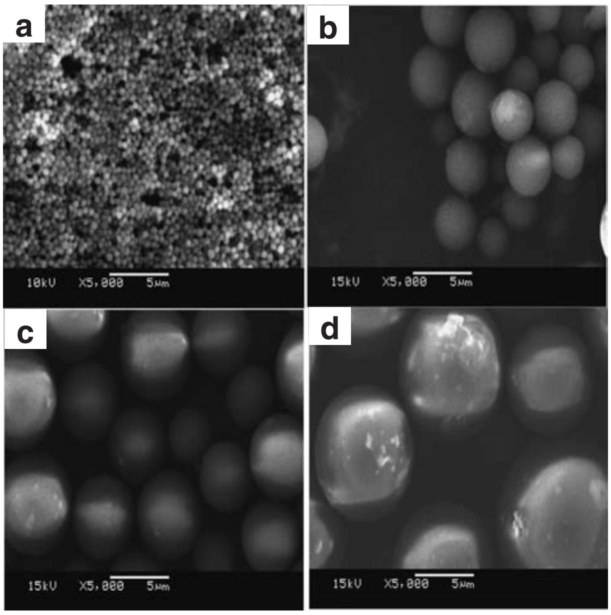

Figure 1. SEM photographs of carbon spheres obtained with different R: (a) 0/4, (b) 0.125/4, (c) 0.25/4, and (d) 0.5/4.

The morphology of carbon spheres prepared at different R was examined with scanning electron microscopy (SEM) observed on a JSM-5600LV microscope, as shown in Figure 1. The image of the products synthesized at $R = 0/4$ indicates that the average diameter of carbon spheres is around 0.5 µm. TEM image of a single carbon sphere shows that surface of it is smooth (Figure S1).[11] The samples prepared at $R = 0.125/4$, 0.25/4, and 0.5/4 are shown in Figures 1b, 1c, and 1d, respectively. These products have a spherical morphology and the sizes of the samples are somewhat nonuniform. The average size and the size distribution of the samples prepared at $R = 0.125/4$, 0.25/4, and 0.5/4 were determined using a SA-CP centrifugal sedimentation size analyzer (Shimadzu) (Figure S2).[11] From the above results, it could be seen that the average particle size of the samples shows increment from about 0.5 to 8 µm, when R is changed from 0/4 to 0.5/4. These results indicate that it is possible to control the particle size by slightly varying R. From EDX spectra of carbon spheres prepared at $R = 0.5/4$, it could be seen that the strong peak was attributed to carbon (Figure S3).[11]

The Fourier transform infrared spectra (FT-IR) of the carbon spheres obtained with different R were measured using a FT/IR-460 Plus spectrometer (JASCO) in KBr, as shown in Figure 2. It indicates that the surface of carbon spheres is hydrophilic, being

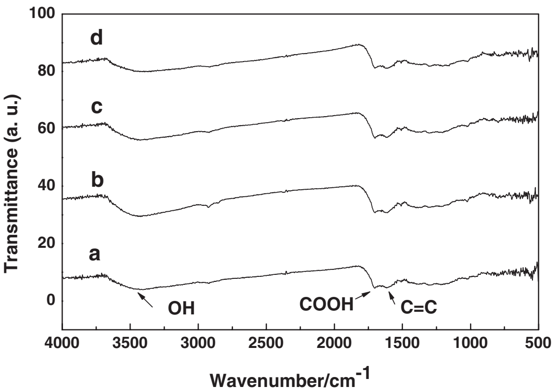

Figure 2. FT-IR spectra of carbon spheres obtained with varying *R*: (a) 0/4, (b) 0.125/4, (c) 0.25/4, and (d) 0.5/4.

functionalized with OH, C=O, and COOH groups, which makes surface modification unnecessary. The peaks between 1000 and 1300 cm^{-1}, which include the C–OH stretching and OH bending vibrations, imply the existence of large numbers of residual hydroxy groups.[7] The adsorption peaks at 1611 cm^{-1} are attributed to C=C double bond vibrations. The adsorption peak at 1704 cm^{-1} belongs to COOH groups.[6,8] Compared with the adsorption peaks, the FT-IR spectra of carbon microspheres prepared at different *R* is unchanged. The elemental analysis (CHN) of the carbon microspheres was carried out using a VarioEL III elemental analyzer (Table S1).[11] The FT-IR and elemental analysis further confirmed that the functional groups of the carbon microspheres were not destroyed by oxalic acid.

In order to further investigate the structure of the obtained carbon spheres, the samples obtained at $R = 0/4$ and 0.5/4 were examined by X-ray diffraction (XRD) measurement on a Rigaku-DMax 2400 diffractometer equipped with graphite monochromatized Cu Kα radiation ($\lambda = 0.15406$ nm). The peak at $2\theta = 21.8°$ in Figure 3 can be indexed to the (002) diffraction of graphite.[9] The broadening nature of the peak is indicative of the highly disordered carbon structures and the presence of amorphous carbon. No obvious difference could be identified from the two patterns.

Althought the exact mechanism of carbon microsphere formation is still unclear, we believe that the formation of the carbon spheres may involve the hydrothermal dehydration of the glucose in the presence of oxalic acid and subsequent polymerization and carbonization of the organic compounds.[6,8] As documented in the literature, acid could promote the dehydration of the glucose under hydrothermal conditions.[10] Also oxalic acid is medium strong acid, and it can decompose into H_2O, CO, and CO_2 by heating, which will not affect the potential applications of carbon spheres. During the hydrothermal process, oxalic acid can be used as acid catalyst to increase the speed of the formation of dehydrated intermediate then to the "carbohydrate-polymer." And it could favor the formation of cross-linked structure of carbon spheres. Therefore, the size of carbon spheres increases dramatically.

In summary, size-tunable carbon microspheres have been successfully prepared by hydrothermal treatment of glucose in the presence of a certain amount of oxalic acid at 180 °C for 12 h. The diameter of carbon spheres increases from about 0.5 to 8 µm, when the molar ratio of oxalic acid/glucose (*R*) is increased from 0/4 to 0.5/4. On the other hand, functional groups of the carbon microspheres prepared by this method remain unchanged. The products may be prepared for application as adsorbents and template materials. Further work is under way to study the formation mechanism and the effect of reaction temperature, reaction time, and concertration of glucose on the size of carbon spheres.

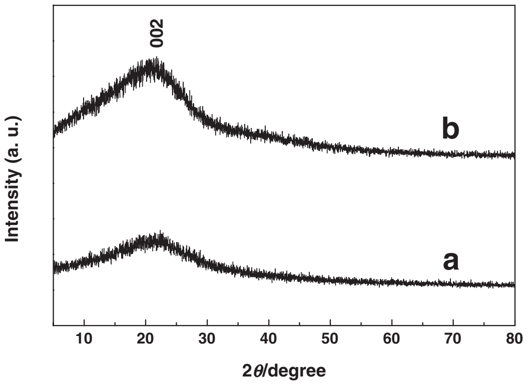

Figure 3. XRD spectra of carbon spheres prepared with different *R*: (a) 0/4 and (b) 0.5/4.

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11 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.