

A Novel Method for the Fabrication of Monodispersed Carbon Nanospheres and Their Crosslinked Forms[†]

Ji-Eun Im, Ha-Na Lee, Jing Li, and Yong-Rok Kim*

Photon Applied Functional Molecule Research Laboratory, Department of Chemistry, Yonsei University, Seoul 120-749, Korea

*E-mail: yrkim@yonsei.ac.kr

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Monodispersed carbon nanospheres (CNSs) were fabricated by a novel method and their structural properties were investigated. CNSs were prepared by the pyrolysis of nanospherical polystyrenes (PS). With the coating of SiO₂ shell, PS particles were effectively separated during pyrolysis process which resulted to CNSs with an average diameter of 40 nm. Moreover, CNSs could be crosslinked with each other through the bondings between the functional groups on their surfaces. Morphology of the fabricated carbon spheres and their crosslinked form were characterized by X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), and fourier transform infrared spectroscopy (FT-IR).

Key Words : Carbon nanosphere, Polystyrene, Silica, Core-shell, Crosslinked form

Introduction

Spherical carbon particles have attracted many attentions because of their applications as electronic devices, supporter of catalysts, adsorbents, and anode materials in lithium-ion batteries, *etc.*¹⁻¹¹ Until now, various methods have been applied for the preparation of homogeneous carbon spheres; ultrasonic treatment, chemical vapor deposition, carbon-arc technique, and pyrolysis of carbon sources followed by hydrothermal method.³⁻¹¹

Among them, the pyrolysis method involves the synthesis of polymer nanospheres and the thermal treatment in an inert atmosphere, resulting to the carbon nanospheres. The advantage of the pyrolysis method is the easy size control of carbon nanospheres (CNSs), which is achieved by a simple size tuning of the polymer spheres. Also, the functional properties of nanoparticles are determined by their shape and size. Therefore, the controlled synthesis of carbon spheres has been focused in many studies of the pyrolysis method. Fujikawa *et al.* reported the pyrolysis synthesis of carbon spheres (160-350 nm) by using resorcinol-formaldehyde polymer as a precursor through heat treatment at 1000 °C.¹² Li *et al.* demonstrated that carbon spheres could be prepared with the diameter of *ca.* 260 nm under 700 °C.¹³ Later, Li *et al.* showed a high temperature method to produce carbon microsphere with size of *ca.* 1.2 μm at 800-1000 °C.¹⁴ Despite of a few successes, the limitation still exists in generating the monodispersed CNSs. It is a difficult job that prevents agglomeration of the particles during pyrolysis process. Therefore, the development of simple and efficient method for the monodispersed CNSs is still being challenged. The discrete and dispersible CNSs are of critical importance for both the fundamental study of carbon colloids

and many practical applications of drug carriers,¹⁵ colloidal catalysts,¹⁶ and nanodevices.¹⁷ In particular, for the applications demanding the large surface area and the uniform morphology, the precise control of monodispersity and particle size which is smaller than 100 nm is of necessity.

In this paper, we report the synthesis of the monodispersed CNSs by pyrolysis of the silica coated polystyrene (PS) nanospheres. By using this approach, the monodispersed CNSs with average diameter of 40 nm are synthesized. The carbon spheres can potentially be controlled by tuning the size of PS particles. The silica coating prevents the PS nanospheres from agglomeration during the pyrolysis process. The results show that CNSs have a very ideal spherical morphology. Moreover, the crosslinked forms are synthesized through the bondings between the functional groups on them. Such crosslinked form of carbon nanospheres may contribute to the improved functionality in catalysis^{1-5,16,18} and energy storage,⁵⁻¹¹ *etc.*

Experimental

The preparation procedure for CNSs is schematically shown in Figure 1(a). The monodispersed PS particles are prepared by microemulsion polymerization. The microemulsion solution consists of 0.1 g of styrene and 0.23 g of DTAB dissolved in 9.85 g of H₂O. The redox initiator was dissolved in the microemulsion. After the microemulsion was bubbled with Ar gas at room temperature for 15 min., the polymerization was carried out at 60 °C for 20 h.¹⁹ PS are coated with a silica shell by hydrolysis reaction with tetraethylorthosilicate (TEOS, 98%) in microemulsion. 480 μg of PS was dissolved in 7.7 mL of cyclohexane. Then, Triton X-100 of 2.98 g, *n*-Hexanol of 1.6 mL, and DI water of 340 μL were added to the cyclohexane solution with a mild stirring for 1 h. TEOS of 100 μL was added to the mixture. After 6 h, aqueous ammonia of 100 μL (28-30 wt %) was added to

[†]This paper is to commemorate Professor Myung Soo Kim's honourable retirement.

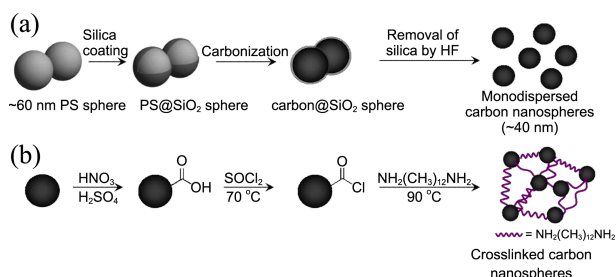


Figure 1. Schematic diagram for preparations of (a) the mono-dispersed CNSs and (b) the crosslinked CNSs.

initiate the TEOS hydrolysis reaction. After 24 h, it was washed and centrifuged with ethanol and DI water.^{20,21} The obtained sample was dried in an oven at 60 °C for 24 h. The carbonization process using tubular furnace (Lenton LTF-14/50/180) was performed under argon flow at 700 °C for 2.5 h (heating rate: 3 °C/min). The aqueous solution (5 wt %) of HF was applied in order to remove the shell of silica.

The synthetic route for preparation of the crosslinked CNSs is illustrated in Figure 1(b). CNSs were suspended in H₂SO₄/HNO₃ (3:1 volume ratio, 4 mL) and agitated by sonication in a water bath for 12 h. After centrifugation, the solid powder was washed with acetone and then dried under vacuum for 24 h at 120 °C. CNSs were stirred in 20 mL of SOCl₂ (containing 1 mL of dimethyl formamide (DMF)) at 70 °C for 24 h. The solid was washed with anhydrous tetrahydrofuran (THF) to remove excess thionyl chloride.

After centrifugation, the remaining solid sample was dried at room temperature under vacuum. Mixture of the resulting CNSs and 0.02 g of 1,12-diaminododecane (melting point, 67 °C to 69 °C) were heated at 90 °C for 96 h. After cooling to room temperature, excess 1,12-diaminododecane was removed by washing it with ethanol four times. The resulting black solid powders was dried at room temperature under vacuum.²²⁻²⁴

Morphology and elemental analyses of CNSs were probed by FESEM (JEOL JSM-6700F) and TEM/EDS (JEOL JEM-3010) equipped with an energy-dispersive X-ray spectrometer.

For TEM measurement, the samples were suspended in ethanol and supported on carbon-coated copper grid. XRD patterns and Raman spectra were obtained with a powder X-ray diffractometer (Bruker D5005, Cu K α ($\lambda = 1.5418 \text{ \AA}$) radiation) and Raman spectrometer (Jobin-Yvon T64000) using an Ar laser of 514.5 nm at room temperature. FT-IR spectra were measured on a Nicolet 360 FT-IR spectrometer.

Results and Discussion

Figure 2(a) shows SEM image of the prepared PS nanospheres with an average diameter of ~60 nm. The PS nanospheres are obtained by microemulsion polymerization of styrene and used as a carbon source for the carbon spheres.

Aggregated PS spheres are formed as methanol vaporizes during the sampling process for SEM measurements. The PS spheres are in the perfect spherical morphology with a diameter of 60 nm. For the silica coating process, aqueous

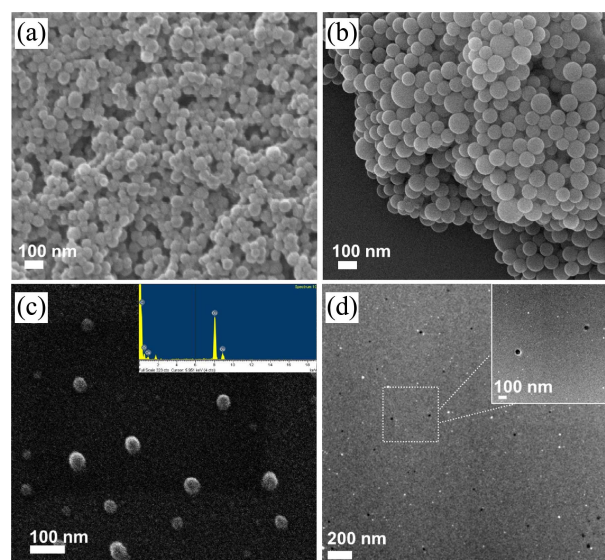


Figure 2. SEM images of (a) PS nanospheres, (b) SiO₂ coated CNSs, (c) The SiO₂ removed CNSs. The inset shows the Energy Dispersive X-ray (EDS) result. TEM image of (d) CNSs. The inset shows the magnified image of CNSs.

ammonia and TEOS are added to PS by a sol-gel reaction. Figure 2(b) shows the SEM image of PS@SiO₂ core-shell spheres that maintain a spherical shape with an average diameter of about 130 nm.

Surface of the PS nanosphere is expected to be a silica shell of about 30 nm in thickness. In order to obtain CNSs, the silica coated nanospherical PS was carbonized and then the silica shell was removed by a HF solution. Figure 2(c) shows SEM image of CNSs. The particle size is 30-40 nm in diameter, which is consistent with the TEM observation in Figure 2(d). SEM (Figure 2(c)) and TEM (Figure 2(d)) images show that the carbon spheres are well monodispersed and have a good quality of spherical morphology. Energy Dispersive X-ray (EDS) analysis in Figure 2(c) indicated the existences of C and Cu, implying that the silica coating was completely removed. CNSs in Figure 2(c) exhibit smaller size compared with the original PS nanospheres shown in Figure 2(a) due to the shrinkage of PS nanospheres during the thermal process.

Raman spectrum in Figure 3(a) presents a strong peak of 1598 cm⁻¹ and a relatively weak peak of 1336 cm⁻¹. The 1598 cm⁻¹ peak (G-band) is associated with the E_{2g} mode of graphite layer²⁵ and the 1336 cm⁻¹ peak (D-band) is attributed to an A_{1g} mode. The intensity ratio of the D and G bands ($I_{(D)}/I_{(G)}$) is 0.85 for CNSs. Figure 3(b) displays XRD pattern of the carbon spheres. The 2θ of two peaks are 22.0° and 43.3° corresponding to the typical graphitic (002) and (100) planes respectively. In the prepared CNSs, the two sharp peaks lie on top of broad band. The interlayer distance of (002) planes was estimated to be 0.406 nm that is larger than that of interlayer distance of graphite ($d_{002} = 0.335 \text{ nm}$). It suggests that the prepared CNSs mostly consist of amorphous carbon with some crystalline graphitic carbon.²⁶

Figure 4(a) shows the SEM image of the crosslinked

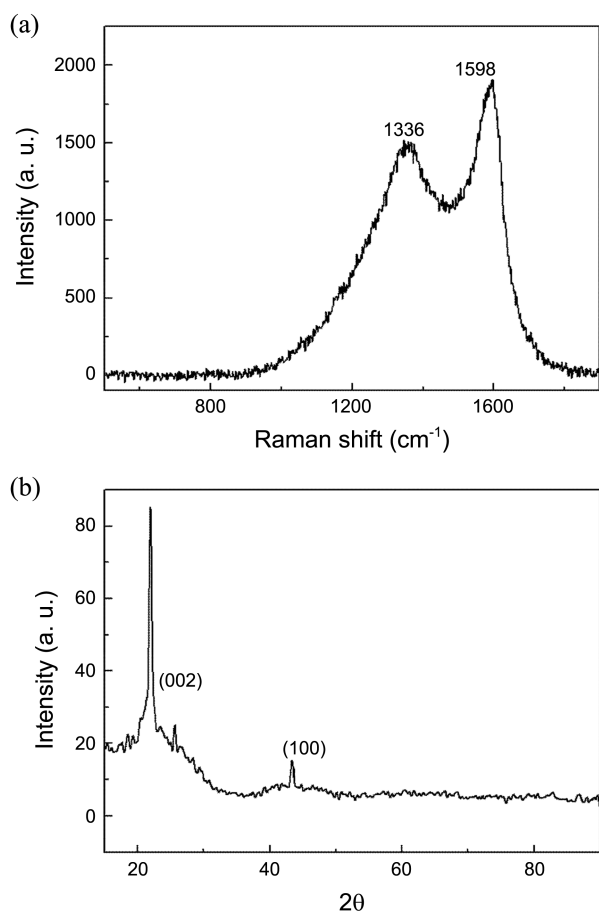


Figure 3. (a) Raman spectrum, (b) XRD pattern of CNSs.

CNSs. It indicates that most of CNSs are crosslinked with each other. The reaction process for the carbon spheres was characterized by FT-IR spectroscopy at each step of the reactions. Figure 4(b) shows FTIR spectra of the pristine CNSs, the acid treated CNSs, and the crosslinked CNSs. After acid treatment of CNSs, a new band appears at 1723 cm^{-1} which is attributed to C=O stretching vibration of the carboxylic acid groups on surface of CNSs. 1,12-diaminododecane molecule as a cross linker has two binding sites. Two amine end groups in the linker have the strong binding ability to the carboxylic group of the acid treated CNSs. They can be crosslinked to the acid treated CNSs via amide binding. Consequently, the crosslinked CNSs exhibit a broad absorption band at $3200\text{--}3600\text{ cm}^{-1}$ due to amino (N-H) groups of the linker, and the peaks at 1334 cm^{-1} and 1650 cm^{-1} are, respectively, assigned to C-N and C=O stretch modes of amide carbonyl groups.^{23,27-29} The bands at 2849 and 2924 cm^{-1} are attributed to the symmetric CH_2 stretch and the asymmetric CH_2 stretch in the linker. Therefore the IR results suggest that CNSs are well crosslinked at the points between the carboxylic acid group of the acid-treated CNSs and the amine group of the linker molecule.

Conclusion

PS-based CNSs were successfully prepared with simple

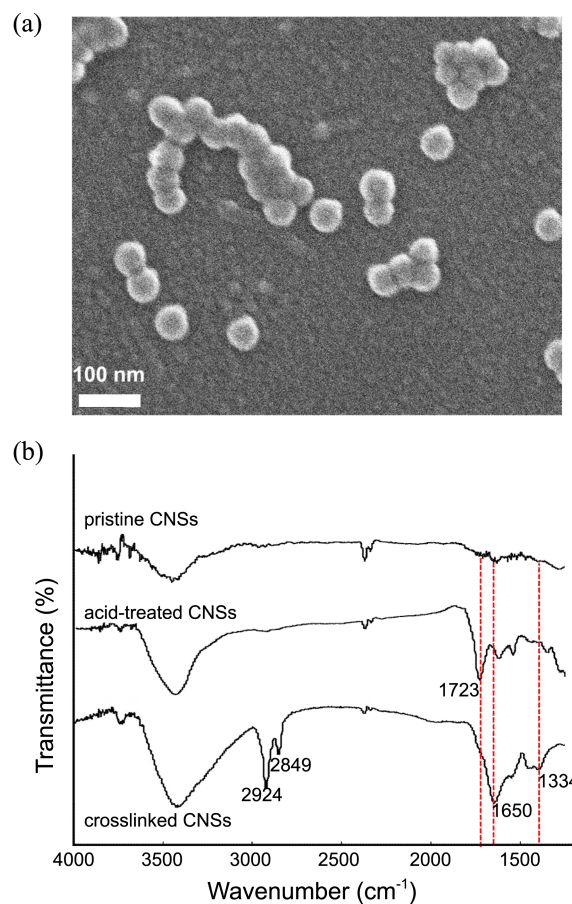


Figure 4. (a) SEM image of the crosslinked CNSs (b) FT-IR spectra of the pristine CNSs (upper), acid treated CNSs (middle), and the crosslinked CNSs (lower).

reactions. By coating the shell of silica, PS particles were effectively protected from agglomeration in the pyrolysis process. CNSs with an average diameter of 40 nm were obtained with homogeneous morphology of spherical shape. Moreover, the crosslinking of CNSs was demonstrated through the surface reactions of the modified carbon spheres. The monodispersed CNSs and their crosslinked morphology are expected to have excellent application possibilities for the fields that require the large surface area and the good and uniform contacts among CNSs.

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