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Synthesis of carbon nanospheres from carbon-based network polymers

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Abstract Carbon nanospheres have been successfully fabricated by simple pyrolysis of a new class of carbon-based network polymers, poly(phenylcarbyne) and poly (hydridocarbyne). The analytic results of morphology and microstructure show that the resultant nanospheres are solid graphite-like balls with the diameter from several tens to hundreds of nanometers. A mechanism based on the carbon nanoparticles self-growth process is proposed for the formation of the nanospheres.

Introduction

Carbon nanostructures have been attracting great interest in the research community because of their remarkable electronic and mechanical properties that could potentially impact many areas of science and technology. Following the discovery of fullerenes [1] and carbon nanotubes [2], new carbon structures have recently been reported. For example, carbon nanofibers [3], carbon capsules [4], carbon nanohorns [5], carbon nanorods [6], and carbon spheres [7–9], etc. have been observed as free-standing structures produced by different techniques. Among the various forms of carbon, spherical carbon structures have recently become an active area of research due to their interesting morphologies and potential applications. Up to now, chemical vapor deposition [10], arc plasma technique [11], catalyzed pyrolysis [12], oxide-catalytic carbonization [13], catalyzed reduction [14], and hydrothermal synthesis [15], etc. have been utilized for the production of carbon spheres. However, owing to metal catalysts may be occasionally included in carbon spheres and preparation needs complicated equipment or rigorous condition (high vacuum or high pressure), the use of the above methods is limited.

A new class of carbon-based network polymers—polycarbynes, $[CR]_n$ (R = Ph, Me, H)—synthesized by Bianconi and co-workers [16–18], are primarily composed of tetrahedrally hybridized carbon atoms, each bearing one substituent and linked via three carbon–carbon single bonds into a three-dimensional random network of fused rings. Among the new network polymers, using $[PhC]_n$ or $[CH]_n$ as precursor, diamond and diamond-like carbon films have been successfully prepared by simple heat-treatment [16, 18–21]. Thus, $[CR]_n$ have been a subject of considerable interest from the scientific and practical application point of view.

Here, we report a novel method for the fabrication of carbon nanospheres from the carbon-based network polymers, by pyrolysis at atmospheric pressure, without the use of any other metal catalyst and template. This method simplifies the preparation of carbon spheres, and makes the process more cost-effective. Moreover, this method enlarges the application of $[CR]_n$ network polymers, which can be made use of fabricating new carbon nanomaterials besides diamond and diamond-like carbon.

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Experimental

The synthesis of $[CR]_n$ (R = Ph and H) was accomplished by the procedure analogous to that used for the synthesis of $[PhC]_n$: the reduction of the appropriate $PhCCl_3$ or $HCCl_3$ monomer, with an ultrasonically generated emulsion of Na–K alloy and an ethereal solvent, tetrahydrofuran (THF) (see Eq. 1).

$$\underset{(\mathrm{R{=}Ph\ and\ H})}{\mathrm{nRCCl_3}} + \mathrm{3n\ NaK} \xrightarrow[\mathrm{THF}]{\mathrm{500\,W,\ 20\,kHz,\ ultrasound}} [\mathrm{CR}]_n + \mathrm{3n\ Na(K)Cl} \tag{1}$$

In an inert atmosphere, glove box equipped with a high intensity ultrasonic immersion pole, anhydrous THF (450 mL) was irradiated at 500 W and 20 kHz power by immersion of the pole, and NaK alloy (50:50 mol%, 18.6 g) was added, followed by 10 min of sonication. A solution of α,α,α-trichlorotoluene (23.0 mL, 0.2 mol) in 40 mL pentane for synthesis of (1) or a solution of chloroform (16.2 mL, 0.2 mol) in 40 mL pentane for synthesis of (2), was then added at a controlled rate over 30 min through an addition funnel, followed by sonication for 60 min. Twenty milliliter of water was added in the reaction mixture drop by drop to quench any unreacted NaK and then water about 250 mL was added, after which the organic layer was separated from the aqueous layer. The organic layer was concentrated to 80 mL in vacuum. For the reaction product of (1), addition of 250 mL of methanol gave a tan precipitate of (1), poly(phenylcarbyne); or for the reactive product of (2), addition of 250 mL of hexanes gave a tan precipitate of (2), poly(hydridocarbyne), which was gravity-filtered and vacuum-dried. The FTIR and NMR analytic results were similar to that reported by Bianconi and coworkers [16–18]. Caution! NaK alloy is pyrophoric and can be explosively reactive, especially with water and halocarbons. Handle with all necessary precautions and in inert atmospheres only.

Freshly prepared powder (1) and (2), respectively, was placed in a ceramic boat located at the middle of a narrow quartz tube, which in turn was placed in a furnace system. The powder was heat-treated by raising the temperature of this furnace to 1000 °C at a controlled heating rate of 5 °C/min in Ar atmosphere, and the oven temperature was maintained at 1000 °C for 4 h. After this treatment, the target carbon spheres were obtained as a black powder. Analysis of the products was performed by Raman spectroscopy, X-ray diffraction (XRD), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDX), and X-ray photoelectron spectroscopic (XPS). The electrical conductivity of the products was measured by a standard four-probe method at the room temperature. Sample tablets (the diameter of 10 mm) used for electrical conductivity measurement were obtained by pressing two kinds of carbon sphere powders using a hydraulic pressure about 10 MPa.

Results and discussion

TEM images of the carbon nanospheres are shown in Fig. 1a–c. It is evident that the carbon spheres obtained from the two polymers have the same surface morphology, which consists of well-defined solid balls (seen in Fig. 1c), and the diameter is in the range from several tens to hundreds of nanometers. The selected area electron diffraction (SAED) pattern consists of well-marked diffraction rings, which corresponds to graphite crystalline nature (seen in Fig. 1d). A typical SEM image for the as-obtained carbon spheres is shown Fig. 2. It is observed that the sample consists of a large number of carbon spheres and a few pieces of amorphous carbon. The proportion of carbon spheres in the sample was 70–75%, which is evaluated from the SEM images. EDX analysis results show no other elements except carbon are present in carbon spheres. In the XRD pattern of carbon spheres obtained from polymer (1) and (2), respectively, shown in Fig. 3a, b, two broad peaks corresponded to the (002) and (101) planes of graphite both can be observed. The broadening of the peaks suggests the possible presence of an amorphous carbon phase within the carbon spheres.

More convincing evidence of carbon materials is provided by the Raman spectra. The visible Raman spectra of

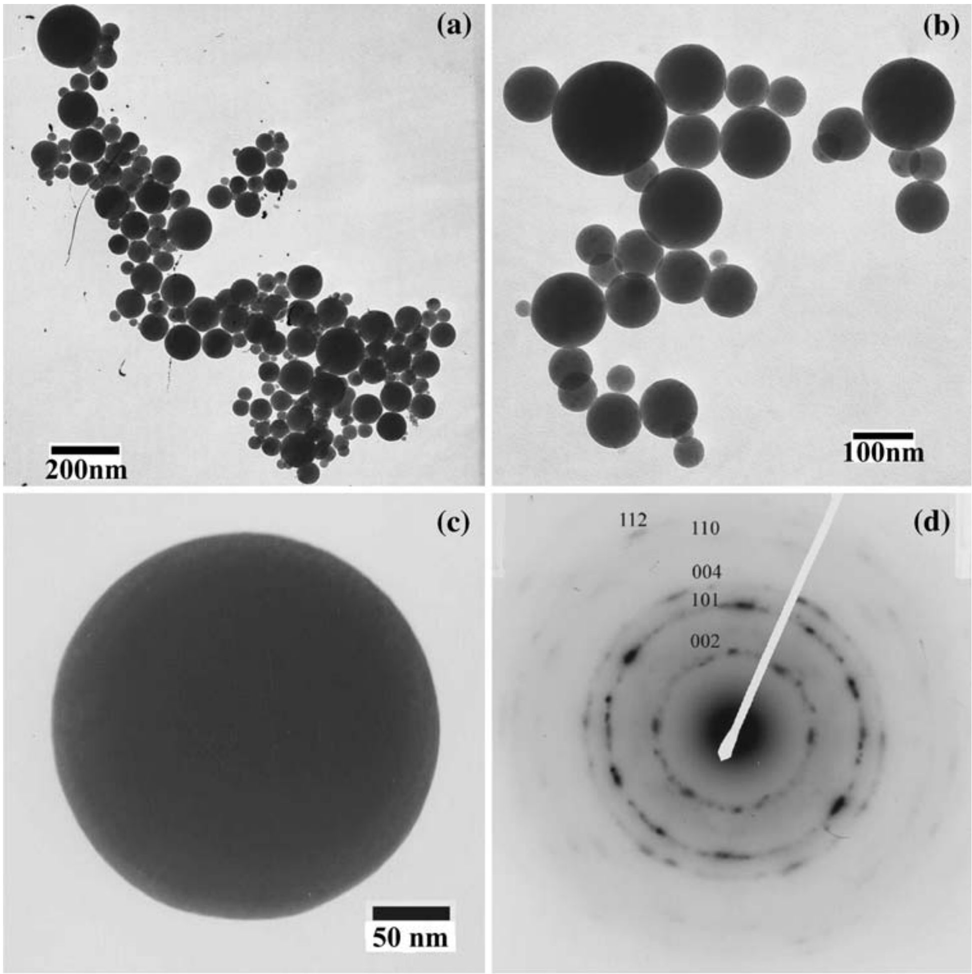

Fig. 1 **a** TEM image of carbon spheres obtained from polymer (1); **b** TEM image of carbon spheres obtained from polymer (2); **c** TEM image of single carbon sphere; **d** Electron diffraction pattern of single carbon sphere shown in **c**

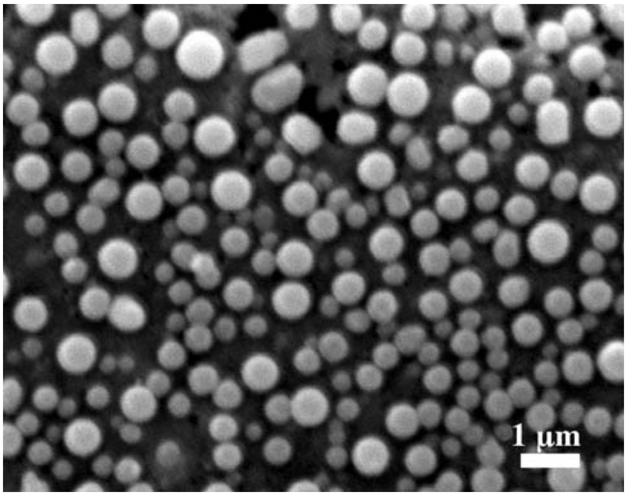

Fig. 2 SEM image of as-obtained carbon spheres

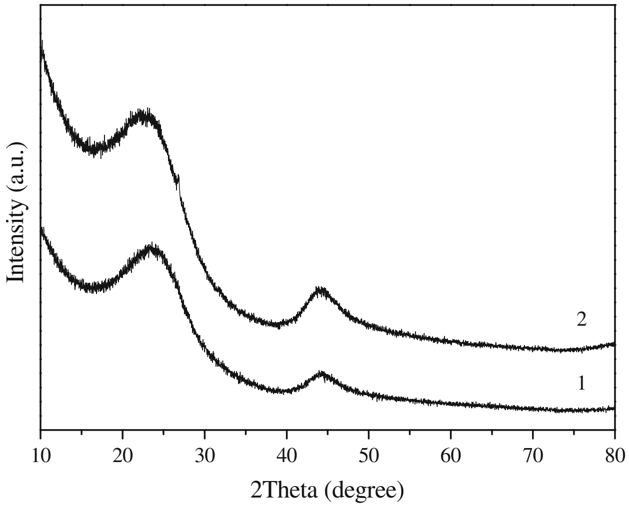

Fig. 3 XRD pattern of carbon spheres obtained from polymer (1) and (2), respectively

carbon spheres obtained from polymer (1) and (2), respectively, are shown in Fig. 4a, b. We can see that the two Raman spectra are identical, in which the G peak (1596 cm^{-1}) attributed to the stretching modes of C=C bonds of typical graphite and the D peak (1347 cm^{-1}) related to the defects and disorders in carbonaceous solid are observed. For the carbon spheres prepared from

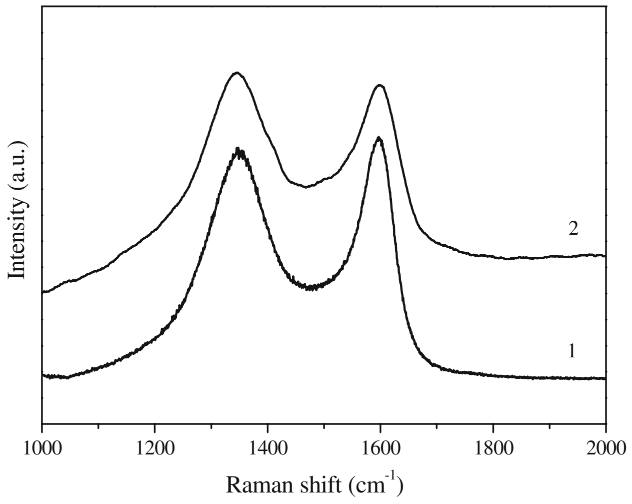

Fig. 4 Visible Raman spectra of carbon spheres obtained polymer (1) and (2), respectively

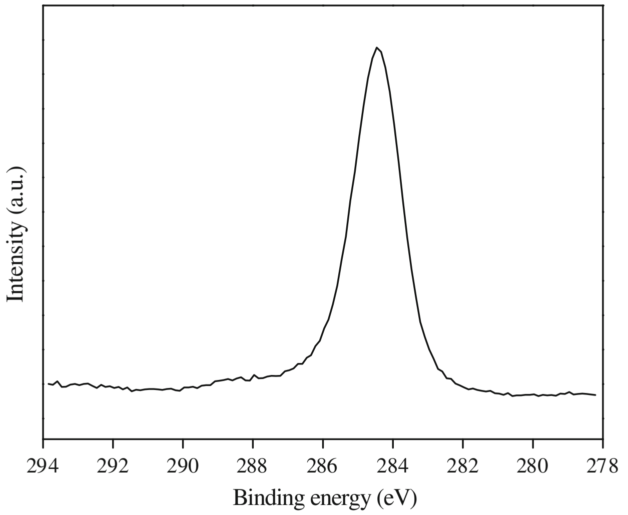

Fig. 5 The C1*s* XPS spectrum of as-obtained carbon spheres

polymer (1) and (2) in the present study, the I_D/I_G value is about 1.8 and 2.0, respectively, implying the graphitization degree of carbon spheres is high. By the XPS analysis seen in Fig. 5, we find that the C1*s* spectrum of carbon spheres shows the same peak centered at 284.4 eV with a full width at half maximum (FWHM) of 1.35 eV, which is the characteristic of graphite. Therefore, we conclude that the carbon spheres have graphite-like structure. The results of electrical conductivity measurement show that the carbon spheres obtained from polymer (1) and (2) have the similar electrical conductivity, for instance, 0.71 S/cm for the carbon spheres form polymer (1) and 0.65 S/cm for the carbon spheres from polymer (2), respectively. Such conductive behavior is mainly attributed to the graphite-like structure.

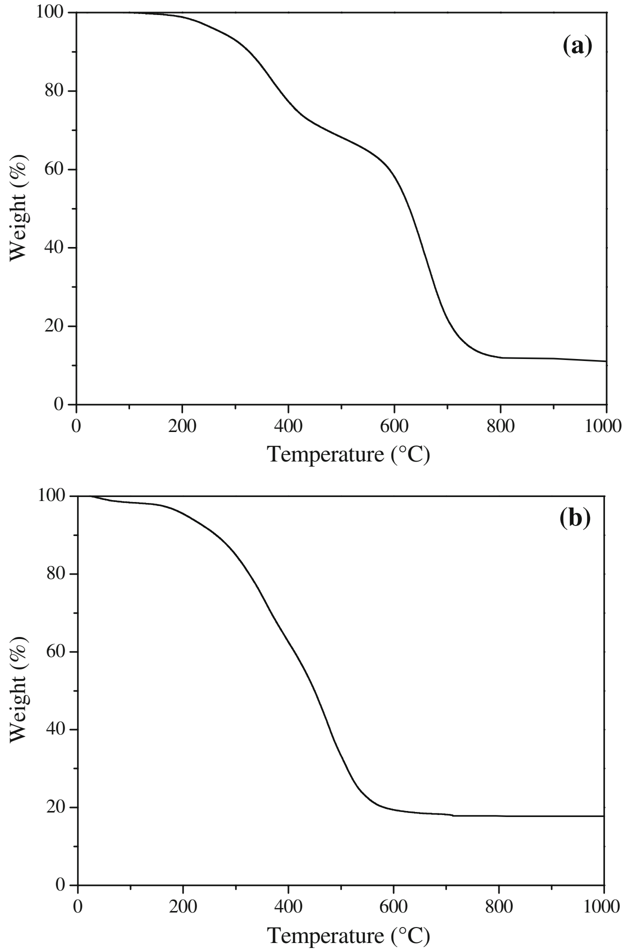

Fig. 6 TGA curves in blowing Ar for polymer (1) (**a**) and polymer (2) (**b**), respectively

The atomic-level carbon network backbone confers unusual properties on the polymers, including $(PhC)_n$ and $(CH)_n$, facile thermal decomposition to form diamond or diamond-like carbon phase at atmospheric pressure [16–19]. Figure 6 showed the TGA curves (the weight loss with respect to temperature) in Ar for polymer (1) and polymer (2). The obvious thermal decomposition of $(PhC)_n$ is complete at 750 °C, having reached an approximately 12% of the initial weight. The weight estimation suggests that all phenyl rings are removed after the heat-treatment. For the decomposition of $(CH)_n$, the loss of 81% completed at 600 °C may be assigned to the loss of H_2 and short-chain gaseous hydrocarbon generated during the heat-treatment. Therefore, when the polymers were heat-treated, phenyl rings in $(PhC)_n$, hydrogen, and short-chain gaseous hydrocarbon generated from $(CH)_n$ could be removed from each polymer network, which cause the structural changes of the polymers and resulted in the conversion of the active *sp*3 and *sp*2 C–C bonded amorphous network from polymer phase. Further, high-temperature annealing may

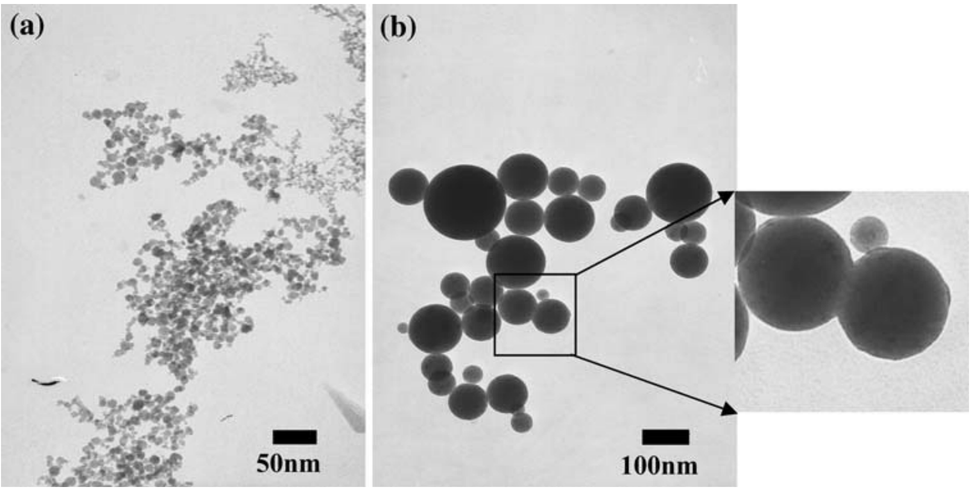

Fig. 7 TEM images of the products prepared by heat-treatment of polymer (2) at 1000 °C for 0.5 h (**a**) and 4 h (**b**), respectively

graphitize the structure. Then, the transition from *sp*3-bonded amorphous carbon to *sp*2-bonded carbon may occur. During this transformation process, though the hydrogen evolved from the polymers may be beneficial to depress the *sp*2 carbon phase and to increase the *sp*3 carbon phase [22–24], the *sp*2 bonding increased and became major bonded-form under the present rapid heating because the *sp*2 carbon phase is more stable in thermal equilibrium condition and the graphitization. Thus, it is proposed that *sp*2 C_n clusters is most probably the reaction intermediate in the formation of graphite-like carbon spheres.

In our experiments, we found that the main products after the heat-treatment of polymer (2) are graphite-like particles in the domain of 1–10 nm with the duration of 0.5 h at 1000 °C (Fig. 7a), while the main products are the target carbon spheres with the duration of 4 h (Fig. 7b). Moreover, it is clear that there are some carbon spheres being just attached on each other, which is well consistent with that reported by Kang and Wang [25]. They demonstrated that the newly synthesized nanosize carbon spheres have high chemical activity, resulting in the accretion of nanosize carbon spheres. They believed that the accretion was directly related to the hydrogen and/or oxygen atoms adsorbed at the edges of the open graphitic flakes distributed at the surface of the carbon spheres. Thus, we speculate that, in our experiments, the edge of individual graphite-like particles with hydrogen atoms on their surfaces could have high chemical activity at high enough heat-treatment temperature. The growth of carbon spheres might start from these individual nanoparticles that acted as nuclei and precursors in the formation process. Furthermore, the fluidity of the nanoparticles is accelerated markedly at the high-temperature annealing. When one carbon nanoparticles approaches another from one side, the hydrogen atoms belonging to the different particle may combine with each other to form H_2, the evaporation of H_2 leaves the carbon atoms, which tend to connect the two particles. By this way, these nuclei then grew uniformly and isotropically to form larger spherical carbon particles in order to reduce surface tension [26]. Further work is definitely needed to study the detailed formation mechanism for carbon spheres with this synthesis, to control the size and to improve the purity of the carbon spheres.

Conclusion

In summary, carbon spheres are fabricated by simple pyrolysis of the new carbon-based network polymers at 1000 °C at atmospheric pressure. In comparison to the conventional syntheses, two features become apparent: (1) the synthetic procedure involves none of the metal catalysts and templates, and makes the process more cost-effective. (2) There is no correlation between the formation of carbon spheres and the substituents, Ph and H groups, of the new carbon-based network polymers. Thus, if the polymer $(CH)_n$ is used as the precursor to fabricate carbon spheres, the as-prepared carbon spheres are absolutely nontoxic enabling their used in biochemistry or biodiagnostics. Furthermore, we anticipate that the synthesis strategy based on the new carbon-based network polymers may be transferred to fabricating other high-quality new carbon nanomaterials such as fullerenes and carbon tubes, with appropriate condition.

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