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A novel approach to carbon hollow spheres and vessels from CCl_4 at low temperatures†

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Carbon hollow spheres (400–600 nm) and vessels (400 nm × 3000 nm) have been synthesized from sp^3-CCl_4 at 190 and 230 °C, respectively. The HRTEM images and Raman spectra reveal the sp^2 nature of the as-obtained products, indicating that the transformation from carbon sp^3 to sp^2 occurs in the reactions. The possible mechanism has also been proposed.

The discoveries of fullerene,[1] carbon nanotubes[2] and close spherical carbon shells[3] as new forms of matter in the nanoscale range have opened a new challenging field in solid state physics, chemistry, and materials science due to their potential applications. Laser vaporization, resistive heating, arc-discharge, and electron irradiation, *etc.*, have been utilized for their production.[1–3]

Recently, the self-assembly template method[4] with hexachlorobenzene as carbon stock and the shock compression technique[5] from C_{60} fullerene have been developed to prepare carbon hollow spheres. Hlavaty *et al.* also used 1-iodohexa-1,3,5-triyne and hexa-1,3,5-triyne to synthesize carbon nanotubes.[6] These methods mostly used sp^2-structural carbon, the basic construction units, as carbon stocks for the synthesis of bucky-carbon materials. To our best knowledge, no report has been published about the preparation of bucky-carbon materials from sp^3-carbon stock at low temperatures. Can sp^3-structural carbon be applied as carbon stock to synthesize bucky-carbon materials at low temperatures? The positive answer will be found in the present communication.

Herein, we provide an approach to prepare sp^2-structural carbon hollow spheres and vessels from sp^3-CCl_4 at low temperatures. The whole process can be formulated as follows:

$$CCl_4 + NaNH_2 \xrightarrow{Co/Ni} \text{carbon hollow spheres/vessels} + NaCl + N_2 + NH_3 + \text{byproducts} \quad (1)$$

Details of a typical experiment are as follows: $NaNH_2$ (0.2 g) and Co/Ni alloy (1.0 g, Co : Ni molar ratio of 1 : 1) were added into a 30 ml Teflon-lined autoclave, which was then filled with CCl_4 up to 90% of the total volume. The autoclave was sealed, warmed up at a rate of 3 °C min^{-1} and maintained at 190 °C for 24 h, and was then cooled to room temperature naturally. The precipitate was filtered off, washed with absolute ethanol, HCl solution (5 mol l^{-1}) and distilled water for several times, and then dried in vacuum at 60 °C for 4 h. The same reactions were also carried out at 210 and 230 °C for 24 h.

Transmission electron microscopy (TEM)‡ images of the samples prepared under different conditions are shown in Fig. 1. Carbon hollow spheres (Fig. 1A) were found to exist in the sample prepared at 190 °C. The proportion of hollow spheres in the sample was 40–45%. It is evident that the boundary of the shell of the hollow spheres is quite well defined. The external diameter of the hollow spheres is 400–600 nm and the thickness of the shells is *ca.* 50 nm. The scanning electron microscopy–energy dispersive X-ray analysis (SEM–EDXA)§ results in Fig. 2 show the composition of the carbon hollow spheres, while the Cu and O energy peaks correspond to the copper disc of SEM and the absorbed oxygen (C : Cu : O = 8 : 4 : 1). In addition, the sample prepared at 230 °C consists of 35–40% of carbon vessels (Fig. 1B). The length and the external diameter of the carbon vessels are 400 and 3000 nm, respectively. The thickness of the walls of the vessels is *ca.* 50 nm and its boundary is also well defined. SEM–EDXA of the vessels also reveals their carbon composition. The yields of hollow spheres and vessels are about 10% and 7%, respectively, calculated from the original reagents.

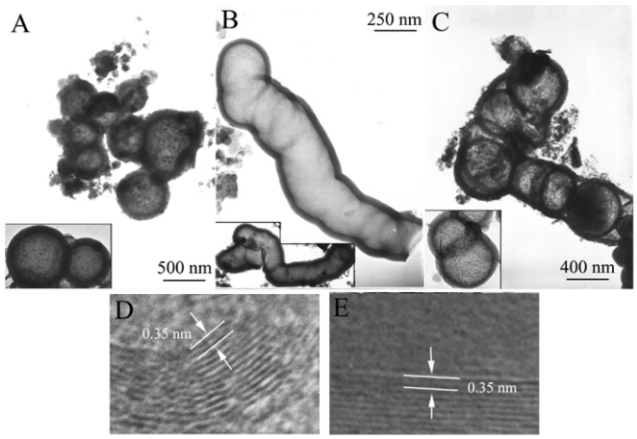

Fig. 1 TEM images of (A) some as-obtained carbon hollow spheres at 190 °C; (B) some as-obtained carbon vessels at 230 °C; (C) some as-obtained aligned carbon hollow spheres at 210 °C. HRTEM images of (D) carbon hollow spheres; (E) carbon vessels.

The direct observation of their structures is determined by high-resolution transmission electron microscopy (HRTEM).¶ Fig. 1D and E show the uniform arrangements of the shells of the hollow spheres and the walls of the vessels. It is obvious that an $sp^3 \rightarrow sp^2$ graphitization process occurred in the reaction. The inter-space between two adjacent layers is around 0.35 nm, which coincides with the *c*/2 lattice parameter of graphite, that is, *d*(0002).

More convincing evidence of carbon materials is provided by the Raman spectra (Fig. 3).‖ The Raman spectrum of the vessels

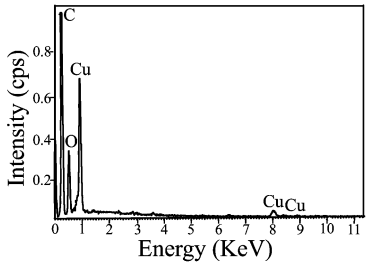

Fig. 2 SEM–EDXA of as-obtained carbon hollow spheres.

† Electronic supplementary information (ESI) available: mass and GC spectra. See http://www.rsc.org/suppdata/cc/b2/b211996j/

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is clearly a doublet at 1580 cm^{-1} (G peak) and 1350 cm^{-1} (D peak) with a ratio of about 1.05, which is characteristic for a disordered sp^2-bonded carbon[7] and similar to the case of carbon nanotubes.[8] On the other hand, the Raman spectrum of the hollow spheres is almost a singlet similar to that of highly oriented pyrolytic graphite (HOPG),[7] indicating that the hollow spheres are in a highly graphitized state. This characteristic has been reported in the literature.[5] Applying the simple Lorentzian approximation, the Raman spectrum of carbon hollow spheres is fit into two peaks. The intensity ratio of the D peak to the G peak, which is related to phonon correlation length for the external diameter of hollow spheres, is 0.01. Using the formula of Knight and White,[9] the external diameter of the hollow spheres is estimated to be 430 nm, close to that found from the TEM image.

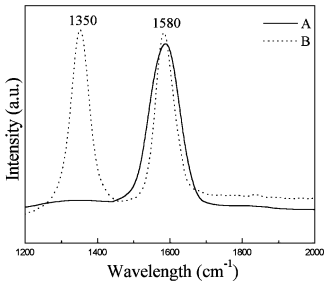
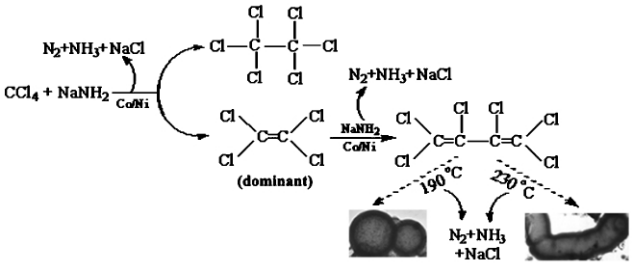


Fig. 3 Raman spectra of (A) carbon hollow spheres, (B) carbon vessels.

The mechanism by which the sp^3-structural CCl_4 produces sp^2-carbon nanostructures is proposed. As a matter of fact, the transformation of $3CCl_4 + 12NaNH_2 \rightarrow$ sp^2-carbon nanostructures + $12NaCl + 2N_2 + 8NH_3$ is thermodynamically spontaneous,[10] due to the large bonding energy of N_2 and crystal lattice energy of NaCl. Especially, $NaNH_2$ has a strong reducing ability[10] and can act as a dechlorination reagent. However, whether sp^2-carbon nanostructures or sp^3-structural products form is still determined by kinetics. The catalysts, reaction temperatures and pH values may affect the reaction process. From the successful experimental results, these factors were well controlled in the present work. The existence of byproduct NaCl can be identified by XRD determination of the raw product without water washing. To investigate the reaction process, we collected 8 ml of filtered solution after reaction, taking the formation of carbon hollow spheres as the example. After removing inorganic compounds, the solution was then determined by gas chromatography–mass spectrometry (GC–MS).** From the gas chromatogram (ESI) corresponding to the mass spectrum, it is found that the filtered solution includes the produced $CCl_2{=}CCl_2$, $CCl_2{=}CCl{-}CCl{=}CCl_2$, a little $CCl_3{-}CCl_3$, unreacted CCl_4 and other compounds with higher molecular weight. It indicates that the sp^2-structural products are favoured over the sp^3-structural ones in the dechlorination reaction. Thus it is proposed that $CCl_2{=}CCl_2$ is most probably the reaction intermediate in the formation of sp^2-carbon nanostructures. It is reported that $CCl_2{=}CCl_2$ species readily couple with each other *via* the dechlorination process.[11] Because the –C=C–C=C– conjugated products are more stable than the compounds with –C≡C– structures, $CCl_2{=}CCl_2$ will couple to the former rather than the latter. Subsequently, –C=C–C=C– conjugated units can continuously be dechlorinated, assembling into carbon hollow spheres and vessels at 190 and 230 °C, respectively. Our previous work[10] has identified the dechlorination and assembly process from $CCl_2{=}CCl_2$ to sp^2-structural carbon materials–multiwalled carbon nanotubes at 200 °C. The $CCl_2{=}CCl_2$ and $CCl_2{=}CCl{-}CCl{=}CCl_2$ detected by GC–MS are the residual intermediates of reactions. In the whole process, the Co/Ni alloy is thought to act as co-catalyst in the dechlorination process. The whole formation path of carbon hollow spheres and vessels is described as Scheme 1.



Scheme 1 Schematic formation path of carbon hollow spheres or vessels.

From the experimental results, one can see that the high temperature leads to the formation of vessels and the low temperature favors hollow spheres. To investigate the effect of reaction temperature on the nanostructures more carefully, the reaction was carried out at the intermediate temperature of 210 °C. It was found that the as-obtained products (Fig. 1C) are some aligned carbon hollow spheres and some of their shells form twins. It indicates that the reaction temperatures are vital for control of the nanostructures, perhaps due to the fact that hollow spheres have less surface strain and need less energy to form.

In summary, carbon hollow spheres (400–600 nm) and vessels (400 nm × 3000 nm) have been synthesized from sp^3-CCl_4 at 190 and 230 °C, respectively. The HRTEM images and Raman spectra reveal the sp^2 nature of the as-obtained products, indicating that the transformation from carbon sp^3 to sp^2 occurs in the reactions. The possible mechanism has also been proposed.

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Notes and references

‡ TEM images were taken on a Hitachi Model H-800 instrument with a tungsten filament using an accelerating voltage of 200 kV.
§ SEM–EDXA were recorded on a JEOL JSM-6700F SEM, in which the solid samples were mounted on a copper disc without any dispersion treatment.
¶ HRTEM images were recorded on a JEOL-2010 TEM at an acceleration voltage of 200 KV.
‖ Raman spectra were recorded at room temperature with a LABRAM-HR Confocal Laser MicroRaman Spectrometer.
** GC–MS were recorded on a Finnigan GC-MS Spectrometer.

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